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SOIL SCIENCE

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SOIL SCIENCE

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ALUMINUM AS A FACTOR IN SOIL ACIDITY

JOSE JISON MIRASOL

University of Illinois

Received for publication June 21, 1920

I. INTRODUCTION

In 1902, the late Dr. Cyril G. Hopkins (33) and his associates of the Illinois Experiment Station presented at the nineteenth annual meeting of the Association of Official Agricultural Chemists the first practical method for ascertaining quantitatively the acidity or lime requirements of a soil. The method is based on the theory that the acids, organic and mineral, in the soil are insoluble in water and cannot be extracted with water, but when a mineral salt solution is added to the acid soil, a double decomposition takes place, the acids (humic acids) react with the salt solution, uniting with the mineral base, forming neutral humates and liberating the mineral acid or an acid salt. The titration of the mineral acid serves as a basis for determining the total acidity of the soil. Eichhorn (16) found that soil rich in humus and containing free humic acids, liberates the acid from neutral salt solutions when brought in contact with such a soil. Solenow (64) also observed that the difficultly soluble organic acids of the humus liberate mineral acids which may affect the plants growing on the soil affected. These observations are at variance with that made by Knop and Detmer (69) who claim that generally "humates" and "humic acids" are much less soluble in salt solutions than in pure water. But Heiden and Schumacker (37) demonstrated that portions of salts in solution are removed by peat, prepared humic acids, and artificial humus when these come in contact with the salt solution. Veitch (80) is also of the opinion "that organic matter is able to remove from solution a portion of the mineral salt with which it is brought in contact," but further asserts that "none of the standard works on absorption of soils makes mention of the production of free mineral acids; neither theoretical considerations nor a cursory examination of the literature lead one to believe that mineral acids in amounts equivalent to the total organic acids are set free by the action of mineral salt solutions on acid organic material."

Shortly after the publication of the Hopkins method of soil acidity-determinations, Veitch (80) subjected it to a critical study. Tests were made for free hydrochloric acid in the extract, and except in one or two cases where the presence of water-soluble sulfuric acid was proven, there were no tests which showed a considerable amount of free acid. Tests for phosphoric acid gave a negative result. In a previous work on the solubility of soil ingredient

in saline solutions, Veitch, however, noted the filtrates were frequently acid in reaction, and attributed it to the presence, in considerable quantities, of aluminum, iron and manganese in the solution. He further found that when the apparent acidity of the extract was equivalent to more than 1 or 2 cc. 0.05 *N* alkali a precipitate was formed on titration which he identified as the hydroxides of aluminum, iron and manganese. Ames and Schollenberger (3) by experiment undertook to demonstrate that free acid is formed by interchange, between acid soils and potassium nitrate solution. The procedure is described in Bulletin 306 of the Ohio Agricultural Experiment Station. The results obtained from 200 cc. of the potassium nitrate extracts are the following:

Acidity due to free acid, by titration with methyl orange.....	9.1 cc. 0.1 <i>N</i> NaOH
Total acidity to phenolphthalein.....	39.9 cc. 0.1 <i>N</i> NaOH
Acidity due to salts of Fe and Al (by difference).....	24.8 cc. 0.1 <i>N</i> NaOH
Chlorine equivalent to 0.3 cc. 0.1 <i>N</i> AgNO ₃	0.0476 gm.
Silica, by loss after HF treatment.....	0.0005 gm.
Ferric and aluminum oxides	0.0471 gm.
Iron by* reduction and titration as Fe ₂ O ₃	0.0136 gm.
Al ₂ O ₃ by difference	0.0335 gm.

The iron was found equivalent to 5.0 cc. of 0.1 *N* NaOH; and the alumina to 19.7 cc.

It is thus seen that although free acid has developed the acidity due to the presence of aluminum is more than twice the acidity due to free acid. The following opinion by Veitch (80) fits well with this result as well as with his own: "It seems that there is no setting free of appreciable quantities of hydrochloric acid, and that there is practically no reaction between the organic matter and the salt solution, whereby difficultly soluble organic acids are dissolved, but that the acidity of the filtrate (or the acidity which is greater than would be given by water under the same condition) is due to the solution of alumina or some other acid-salt yielding base."

The author has also made some studies on the composition of potassium nitrate extracts of three acid soils. A more detailed account of the results of this study will be given in the latter part of this paper, but the conclusion he reached is that potassium nitrate solution brings into solution the aluminum in the acid soil when the latter is brought in contact with the salt solution; that the strong acidity exhibited by the potassium nitrate extract is due largely to the presence of a considerable amount of aluminum in solution; and that the precipitate formed at the point when the extract passed from an acid into an alkaline solution is largely aluminum hydroxide.

Hitherto, the significance of Veitch's discovery has never been appreciated, and the nature of soil acidity has generally been ascribed to the presence of free organic and mineral acids in the soil. The recent work, however, of such men as Abbott, Conner and Smalley (1) of Indiana, Ruprecht and Morse of Massachusetts (59) and Hartwell and Pember (27) of Rhode Island, in which they have shown the rôle aluminum plays in some acid soils, has given a new phase to the problem of soil acidity. The last two men, especially, are so

convinced of the presence of aluminum in acid soils as the cause of the different behavior of barley and rye grown in an acid soil that they think "the elimination of the effect of aluminum in acid soils seems likely to prove more important than the neutralization of the acidity" and that "attention should be given to methods of determining active aluminum while we are also developing those for soil acidity" (28). If aluminum should prove to be the most important factor in acid soils, and a search is made for a method for determining active aluminum and for eliminating its effect in acid soils, such a method already exists. Veitch had demonstrated that the Hopkins method does not bring considerable free acids in an acid soil into solution but instead brings the aluminum in the soil into solution; the application of the method to field conditions has brought excellent results. In other words, the method determines aluminum. The application of limestone to acid soils, according to the method, eliminates the effect of aluminum, and so far as aluminum is concerned in acid soils the Hopkins method is the best method for determining and correcting soil acidity.

II. OPINIONS CONCERNING THE CAUSE AND NATURE OF SOIL ACIDITY

Frear (19) and Ames and Schollenberger (3) have already reviewed quite comprehensively the literature and theories covering the subject of soil acidity and in this paper the author only attempts to summarize briefly the opinions expressed by the different investigators. These opinions or theories may be divided into three groups.

1. The presence of true acids.
2. Adsorption by soils.
3. The presence of considerable quantities of soluble aluminum salts.

1. The presence of true acids

In this group there are two important theories, the organic acid theory and the mineral acid concept. Let us take up first the organic acid theory.

In the decomposition of plant and animal residues organic acids are produced. Under proper aeration these decomposition products are used up by soil organisms as fast as they are formed. But in poorly aerated and drained soils, these products may accumulate giving rise to acid condition. The acidity of some peat and muck soils has long been known, and this acidity has been assigned to complex insoluble organic acids. This theory was proposed by Sprengel (65) after having discovered what he called humic acid. Berzelius (6) further advanced the theory when, by treating a soil with an acid he obtained two substances, one insoluble and the other soluble, the latter being identical to the humic acid of Sprengel. Tacke and Sückting (71) held the view that the acidity of humic acids can only be accounted for on the basis of true acids. That organic acids exist in normal soils is a known fact. Blair and Macy (8) in Florida found muck soils which gave an acid aqueous extract

after boiling the extract for a long time. They ascribed the acidity to soluble organic acids in the soil. The so-called humus has been subjected to a critical examination by Shorey (63) who found thus far at least thirteen organic acids, among which are oxalic acid, succinic acid, saccharic acid, acrylic acid, picoline carboxylic acid, paraffinic acid and lagnoceric acid. But it is believed that under ordinary conditions the organic substances present in the soil cannot bring a condition unfavorable to plant growth.

Some soils while deficient in organic matter are decidedly acid, hence it follows that the acidity in this case must be attributed to other causes. Truog (75) thought that the acidity in this case is caused by true acids. It is claimed that plants and certain hydrated compounds in the soil removed the bases from the salts leaving free acids. Stoddart (67) for example, is of the opinion that the sulfates and chlorides in the soil are split up, the base elements being absorbed by the plants, leaving the acid radicals as acids thus giving rise to an acid condition. It is further believed that the silicates which are important constituents of soils of non-limestone rock origin are decomposed by carbonated water in the soil resulting in the removal of bases which are either taken up by plants or leached out. The oxides of silicon and aluminum left over combine to form aluminum-silicic acids which may cause soil acidity. Truog (77) says: "It is possible that mere removal of bases from the original silicates may give rise to acid silicates which cause soil acidity." On this point Hopkins (32, p. 176) says, "Acid silicate is formed from polysilicates from which some basic elements may have been removed and replaced with acid hydrogen, by reaction with soluble organic acids, or possibly by the long-continued weak action of drainage waters charged with carbonic acid, do exist in the soil, and the evidence thus far secured indicates that they account for most of the acidity of soils which are at the same time strongly acid and very deficient in humus." In the study of acid red clay soils of Porto Rico, Loew (41) ascribes the acidity to the presence in the soils of an acid clay or aluminum silicates having the formula $H_4Al_2Si_2O_9$, which he called argillic acid.

Lastly by the use of electrometric and colorimetric methods of determining hydrogen-ion concentration, Gillespie (22) demonstrated the presence of acid in the soil. His findings were in accordance with the results of Sharp and Hoagland (62), who concluded that soil acidity is due to the presence of an excess of hydrogen ions in the soil solution.

It is believed that certain treatments of the soil may also give rise to acidity in the soil. Continued application, for example, of artificial fertilizers like sulfate of ammonia and acid phosphate causes acidity of the soil. When sulfate of ammonia is applied to soils, ammonia is nitrified leaving the sulfate radical to form sulfuric acid. Muriate of potash, according to Stoddart (67) tends to leave an acid residue due to the absorption of potassium by plants or soil colloids, leaving free sulfuric and hydrochloric acids. There are instances in which continued application of ammonium sulfate to the soil resulted in an acid soil. Wheeler (82) reported acid the soil in the plots of the Rhode

Island Experiment Station which received ammonium sulfate continuously. Hall and Gimingham (24) in England, Hunt (35) in Pennsylvania and Ruprecht and Morse (60) in Massachusetts encountered similar results with experimental plots receiving ammonium sulfate continuously but not limed.

It has also been thought that acid phosphate may produce acidity in the soil. The fact that acid phosphate is an acid salt is responsible for this belief. In discussing the advantages of raw phosphate over acidulated phosphate Hopkins (32, p. 242) says: "A third point in favor of raw phosphate in common with bonemeal and slag, is that it is free from acidity and has no tendency to injure the soil. This is a minor advantage, because if acidity develops from the use of acid phosphate (and it does) it can be corrected at a small expense by the addition of any form of lime." Thorne (72) of the Ohio Experiment Station also is of the opinion that acid phosphate may develop acidity in the soil. He says: "There is reason to believe that acid phosphate increases the tendency to soil acidity, but it is not the sole cause of such acidity for there are very acid soils which have never received any phosphate." These opinions, however, do not agree with the experimental evidence. In a study of the acidity of experimental plots in Indiana in which acid phosphate has been applied for twenty years, Conner (13) found that these plots show less acidity than soils which have never had acid phosphate. By computing the amount of free phosphoric acid added to the soil when the rate of application is 200 pounds of acid phosphate containing 14 per cent available phosphoric acid, Frear (19) concluded that it would take a long time and a large amount of phosphate to make a soil acid by such direct action. The results of the author's tests which will be presented in this paper also indicate that acid phosphate tends to reduce rather than increase the acidity of the soil.

2. *The adsorption theory of soil acidity*

The phenomenon of soil acidity has also been explained as a case of adsorption. Cameron (11) was the first to apply the theory of adsorption in explaining the acid reaction of certain soils. He attacked the blue litmus paper test for soil acidity on the ground that wet cotton also turns blue litmus paper red. He is of the opinion that the reddening of blue litmus paper by certain soils is a case of selective adsorption.

After investigating some acid soils of Michigan, Harris (25, 26) arrived at the conclusion that the acid reaction of the soil is due to selective adsorption and not to the presence of acids.

Parker (49) asserts that because of the nature of the surface of its constituents soils adsorb the cation at a greater rate than the anion, and that the acid reaction of certain soils is due to this fact.

In a comprehensive study of acid soils of Japan, Daikuahara (14) concludes that their acid reaction is not due to organic acids (humus) alone but also to adsorption of colloidal compounds of aluminum and iron.

Gully (23) also ascribes the acid reaction of peat moss and peat soils to adsorption of the colloidal matter of the covering of the sphagnum cells.

3. The presence of soluble salts of aluminum in the soil

The idea had its inception in the work of Abbott, Conner, and Smaller (1) who investigated a few years ago, the causes of the unproductivity of some soils in Indiana. They obtained water extract of the acids soils, and determined its composition. They have found that the extract reacts acid to phenolphthalein and that the nitrate was present partly as aluminum nitrate. Corn seedlings were grown in the extract along side of solutions of nitric acid and aluminum nitrate of known normality, and it was found that the extract was extremely toxic up to 0.0005 *N*. It was found that the toxicity of the extract was equal to the toxicity of nitric acid and aluminum nitrate of the same normality; and the conclusion arrived at was that soluble salts of aluminum are largely responsible for the unproductiveness of the soils in question.

Ruprecht and Morse (60), investigating the effect of continued application of ammonium sulfate to soils, found that aluminum sulfate is formed which causes the acid reaction and the unproductivity of the soil.

Hartwell and Pember (27) carried on a comprehensive search for the cause of the different behaviour of rye and barley grown on soils from plots continuously receiving ammonium sulfate. Different inorganic substances have been subjected to experiment to discover the most active factor and the conclusion reached was that aluminum is the element responsible for the depression of the growth of barley.

After reviewing the different theories concerning the nature and cause of soil acidity Ames and Schollenberger (3) expressed the following opinion: "The theory of the existence of silicic or alumina-silicic acids in the soil would serve as a complete explanation for all the observed phenomena; the conception is simple and is supported by analogy with better known reactions which is as much as can be said for any of the theories which have been offered."

The work of Abbott, Conner and Smalley, Ruprecht and Morse, and of Hartwell and Pember, however, has opened up new possibilities by which the nature and causes of soil acidity could be studied further. With the hope that more light might be thrown upon aluminum as a factor in soil acidity the present work has been undertaken, bearing in mind three facts. First, aluminum salts are highly toxic at a certain concentration; second, aluminum is abundant in the soil, being next to oxygen and silicon; and third, plants absorb bases and calcium carbonate is leached out of the soil resulting in the depletion of the soil of this compound and enabling the aluminum in the soil to act as a base.

III. ALUMINUM IN AGRICULTURE

Aluminum is universally known as a non-essential element to plants. Hydrated silicates and oxides of aluminum, however, are believed to exercise great influence in holding some of the plant-food elements in the soil, preventing their loss in drainage water. Aside from this, aluminum has no economic

value in agriculture. As stimulants or as fertilizers very little is known of aluminum compounds and the few scattered experiments on this subject are incomplete and inconclusive. On the other hand, aluminum has been found extremely toxic to plants. Since aluminum is abundant in the soil and under certain conditions becomes harmful to plants, as in the case of some acid soils, it is in this fact that aluminum will prove of great importance to the agriculturist.

Aluminum in plants

Although aluminum is not an essential element, analyses of ashes show that it is taken up by plants. It is, however, present in small amounts in most plants. Pfeffer (50) speaks of the abundance of aluminum in *Lycopodium chamaecyparissus* and *L. alpinum*, where it constitutes from 22 to 27 per cent of the ash, while in certain species of *Lycopodium* only traces are found. Johnson (37) states that aluminum is found in small amounts in the ashes of agricultural plants, but added that it is not clear whether it is an ingredient of the plants or due to particles of clay adhering to plants. Robinson, Steinkoenig and Miller (57) report analyses of legumes, vegetables, grasses, trees, shrubs, and show that aluminum is found in all the plants analyzed. The form in which aluminum is present in the plant is not known. According to Berzelius, aluminum as alumina is united with tartaric acid, and according the Ritthausen with malic acid [quoted by Johnson (37)]. Pfeffer (50), however, is not certain whether aluminum in *Lycopodium* is present in the form of tartrate. In a study of the aluminum contents of certain vegetables including corn and corn products, hominy, oatmeal, carrots and white and sweet potatoes, Meyers (44) found that aluminum in these vegetables is found in a soluble form, and averred that a relatively large consumption of aluminum may result from a diet consisting chiefly of vegetables.

Physiological action of aluminum on plants. According to Jost (38) Jamano found aluminum to be of service in the development of barley. This is in conflict with the results of Hartwell and Pember (27), in which they show that the depression of the growth of barley in an acid soil is due to the presence of aluminum. Maze (43) also asserts that aluminum is necessary for the best growth of maize. Experimental evidences, however, point to the fact that aluminum is not only a non-essential element but it is also very harmful to plants under certain conditions.

Fluri (18) describes certain experiments carried out on *Spirogyra*, *Elodea*, and *Lemara* with sulfate, nitrate, chlorate and bichromate of aluminum. He found that in light, production of starch is reduced, but also found that while assimilation was checked it was not inhibited. The aluminum found in the cell was small and the action could not then be attributed to a chemical reaction. But as starch production was affected it was thought that the action of aluminum was on the diastase.

Hebert (29) made some germination tests of peas, wheat and rape with sulfates of aluminum and other metals and found that the salts were strongly

poisonous. Varvaro (79) also reports that aluminum oxide, like the oxides of manganese, iron, uranium, cerium, copper, zinc, cadmium, mercury and lead has a retarding effect on the germination of kidney beans, but has an accelerating effect in the case of corn. Experimenting on the effect of different aluminum salts on the germination of wheat, Micheels and DeHeen (45) found that while kaloin and alumina were somewhat beneficial, the salts were very harmful.

In investigating the effect of different salts of aluminum on the growth of *Zea mays*, *Vicia faba*, *Leus esculenta* and *Helianthus annuus* Kratzmann (39) found that the growth was hindered by the salts when the concentration was 0.005 per cent, but stimulated when the concentration was only 0.0001 per cent. Aluminum nitrate showed a toxic effect. In this connection, significant is the statement of House and Gies (35) that the toxicity of aluminum salts depends upon the concentration of the solution. Yamano (84) found that moderate amounts of aluminum salts have a stimulating effect upon the development of barley and flax. He further found that in water culture 0.2 per cent of alum proved injurious after three weeks while 0.8 per cent killed the plant in a few days. Miyake (46) also found that the aluminum chloride is toxic even in dilute solution. The toxicity appeared when the concentration was greater than 0.000133. It was further found that the toxicity of aluminum chloride was approximately equal to that of hydrochloric acid of the same normality. Under the supervision of Professor C. F. Hottes of the Department of Plant Physiology, the author carried on some experiments on the toxicity of aluminum sulfate to barley. Solutions of 0.01 *N*, 0.001 *N*, 0.0001 *N*, and 0.00005 *N* were prepared, and barley seedlings were grown in them. The author found that the average growth of 10 plants for 7 days was 70.5 mm. in the control; 45.5 mm. in 0.01 *N*; 65 mm. in 0.001 *N*; 71.5 mm. in 0.0001 *N* and 78.9 mm. in 0.00005 *N*. It is thus seen that 0.01 *N* is highly toxic; 0.001 *N* depresses growth; and 0.0001 *N* has no effect at all. In 0.00005 *N* stimulating effect was noted. It was further observed that the seedlings growing the first two dilutions had root systems more than three times as greatly depressed as those growing in the control or in any of the two weaker solutions. The limit of toxicity lies probably between 0.0001 *N* and 0.001 *N*.

Other investigators who have proved the toxicity of aluminum salts are Abbott, Conner and Smalley; Ruprecht and Morse; and Hartwell and Pember, whose works have been already mentioned in the preceding discussion. It may be said, however, that it was not until the work of these men appeared that the toxicity of aluminum salts has been linked with the soil as a contributing factor in soil-acidity.

Aluminum salts as stimulants and fertilizers

Experiments have been made to ascertain the value of aluminum salts as catalysts or stimulants. Pfeiffer and Blanck (51) found that small amounts of aluminum sulfate combined with a small portion of manganese sulfate

caused an increase in the yield of dry substance in the grain, but an increase of the salt reduced the yield. Stoklasa (68) reports results from experiments on catalytic fertilizers for sugar beets. He showed that a combined application of 9 kgm. (19.8 lbs.) of manganese and 4.48 kgm. (9.8 lbs.) of aluminum sulfate per hectare has increased the yield of sugar beets from 30 to 50 per cent. He is of the opinion that aluminum, like manganese, zinc, and copper, is a catalytic agent, performing a function in the assimilation of carbon by promoting rapid photosynthesis. Boullanger (9) made a comparative study of the catalytic value of the sulfates of aluminum, manganese, ferrous iron and uranium, and found that while the results obtained were not uniform, in the majority of cases they increased the yield. In the case of aluminum nitrate, however, the experience of Munerate, Mezzadroli and Zapparole (47) was different. They carried on a comparative test of the stimulating value of aluminum nitrate and sulfate together with the sulfate, chloride, dioxide and carbonate of manganese, boric acid, borate of soda and sulfate of uranium. The results showed that the lowest yield of sugar beets was obtained in the plot which received 100 kgm. (220 lbs.) per hectare of aluminum nitrate.

An attempt has been made also to find the effect on the productivity of the soil by the application of aluminum silicates. Voelcker (81) reports pot culture experiments in which green manures were associated with aluminum silicates, sodium silicates, kaolin, lime and magnesia. The results obtained showed that kaolin did not increase the yield of crops, but aluminum silicates with mustard as a green manure caused a large increase in the crop.

Finally, experiments have been carried out to determine the value of insoluble aluminum phosphate as a source of phosphorus to the plants. Pranišnikov (52) describes sand culture experiments in which wheat, oats, barley, peas and buckwheat were fertilized with aluminum phosphate alone and with calcium carbonate. The conclusion reached was that aluminum phosphate is assimilated, and that calcium carbonate had no appreciable depressing effect on the assimilability of aluminum phosphate. Baguley (4) reports a comparative test of orthophosphates of iron, calcium and aluminum on oats, peas and Swedish turnips grown on sand and chalk. The results obtained were better with iron and aluminum phosphates than with calcium phosphate. Truog (74) also presents results of experiments carried out in the greenhouse with ten different kinds of plants manured with rock phosphate, precipitated calcium phosphate, and phosphate of aluminum, iron and manganese. The results obtained were summarized as follows: "Contrary to the general belief that aluminum and iron phosphates are relatively unavailable to plants, nine of the ten plants tested made better growth on aluminum phosphate than on calcium phosphate, and six better growth on iron (ferric) phosphate." In another publication (76) in which results from a more comprehensive series of experiments on phosphate involving a large number of plants, were presented, he draws this conclusion: "Precipitated ferric and aluminum phosphates produced with a few exceptions good growth and in a few cases even better growth than the acid phosphate."

Aluminum in the soil

Aluminum is the most widely scattered metal (53) and next to oxygen and silicon is the most abundant element. It constitutes 7.85 per cent of the lithosphere and 7.30 per cent of the lithosphere and atmosphere combined (12). It does not occur in nature in the free state, but in combination with oxygen, the alkalies, flourine, silicon, the acids, etc., it forms minerals and rocks which on disintegration become the bases of soils and clays. Aluminum is present in the soil as the oxide, hydroxide, hydrated oxides, phosphate and silicates (64). In order to give some idea as to the amount of aluminum present in the soil, analyses of some soils in America are given in table 1.

TABLE 2
Chemical analyses of some American soils

CONSTITUENTS	ADOBE SOILS		COASTAL PLAINS PROVINCE	LIME-STONE VALLEY AND UPLAND PROVINCE	PIED-MONT PLATEAU PROVINCE	GREAT PLAINS PROVINCE	GLACIAL AND LOESSIAL PROVINCE	RIVER FLOOD PLAINS PROVINCE
	A	B						
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
SiO ₂	19.24	66.69	94.50	79.25	66.49	78.85	76.81	93.29
Al ₂ O ₃	3.26	14.16	2.07	8.89	17.11	9.68	9.73	2.45
F ₂ O ₃	1.09	4.38	0.83	4.44	7.43	2.72	3.26	0.78
MnO.....	Trace	0.09	0.007	0.07	0.51	0.036	0.068	0.066
MgO.....	2.75	1.28	0.09	0.33	0.31	0.72	0.60	0.01
CaO.....	38.94	2.49	0.39	0.63	0.36	0.94	0.92	0.15
Na ₂ O.....	Trace	0.67	0.11	0.24	0.16	2.02	1.74	0.03
K ₂ O.....	Trace	1.21	0.10	0.67	0.62	2.31	2.20	0.45
H ₂ O.....	1.67	4.94						
P ₂ O ₅	0.23	0.29	0.06	0.18	0.17	0.11	0.12	0.06
CO ₂	29.57	0.77						
Organic matter.....	2.96	2.00	1.13	1.96	1.26			
SO ₃	0.53	0.41	0.07	0.13	0.07	0.07	0.11	0.10
Cl.....	0.11	0.34		1.74	4.80	8.06	2.28	4.09
Loss on ignition.....								2.12

The first two columns are adopted from Clarke (12), the next three from Robinson (55) and the last three from Robinson, Steinkoenig and Fry (56). The soil indicated A, is from Salt Lake City, Utah; B is from Santa Fe, New Mexico; No. 1 is Norfolk sandy loam, 3 miles southwest of Laurinburg, North Carolina, depth 0 to 14 inches; No. 2 is Decatur clay loam, 1 mile east of Hollywood, Alabama, depth 0 to 4 inches; No. 15 is Cecil clay 2½ miles northwest of Charlotte, North Carolina, depth 0 to 6 inches; (1) is Colorado sand near Greeley, Colorado, depth 0 to 14 inches; (5) is Knox silt loam, 2 miles north of Farley, Missouri, depth 0 to 14 inches; and (13) is Cahaba very fine sandy loam, Minden, Louisiana, depth 0 to 12 inches. For further details about these soils the reader is referred to the publications of these men.

By recalculation the total aluminum in these soils per acre of 2,000,000 pounds of surface soil amounts to 34,576 pounds for Salt Lake City adobe; 151,181 pounds for Santa Fe adobe; 21,954 pounds for Norfolk sandy loam, North Carolina; 94,237 pounds for Decatur clay loam, Alabama; 181,469 pounds for Cecil clay, North Carolina; 102,666 pounds for Colorado sand; 103,196 pounds for Knox silt loam, Missouri; and 25,985 pounds for Cahaba very fine sandy loam, Louisiana.

Burd (10) also reports total analyses of certain silty clay loam and fine sandy loam soils in California in which, for example, one silty loam soil and one fine sandy loam soil contain 14.03 per cent and 16.73 per cent alumina, or 148,802 pounds and 177,438 pounds aluminum per acre, respectively.

Alumina in the subsoil. Analyses of the subsoils of soils given in the preceding table show larger quantities of aluminum. For example, the subsoil of Decatur clay loam contains 3 per cent more alumina than the surface soil. In every one of the ten subsoils analyzed by Robinson (55) alumina is higher than in the surface.

TABLE 2
Alumina in soil separates

SEPARATES	HEAVY LOAM	LOAMY LOESS	COARSE SANDY GNEISS SOIL
		per cent	per cent
Coarse dust, 0.25 to 0.01 mm.....	1.63	7.28	18.71
Medium dust, 0.01 to 0.005 mm.....	15.20	14.20	24.20
Fine dust, 0.005 to 0.0015 mm.....	20.48	19.41	30.21
"Clay" (Schlamm), 0.0015 to 0 mm.....	27.76	29.97	32.42

Distribution of aluminum in the soil separates. There have been a few attempts to determine the distribution of the chemical constituents of the soil in the different soil separates. Puchner, quoted by Failyer, Smith and Wade (17), presents data of chemical analyses for separates of three types of soil. The percentage of alumina found is given in table 2.

Steinkoenig (66) also reports determination of certain constituents of separates of ten loam soils from New York, North Carolina, Pennsylvania, South Carolina, Virginia, New Hampshire and Wisconsin. The average alumina found in the separates of these soils, together with the maximum and minimum is given below:

	FINE SAND	COARSE SILT	FINE SILT AND FINE CLAY
	per cent	per cent	per cent
Average.....	5.48	8.44	22.57
Maximum.....	12.56	18.28	31.33
Minimum.....	0.40	1.48	16.76

From the data above it can be seen that the largest quantity of aluminum is found in the finest particles of the soil and that the quantity diminishes as the particles become coarser. It follows from this fact that the more clayey the soil is the higher is the aluminum content, and this seems to be the case if the Cecil clay is taken as proof.

The aluminum compound in the soil that gives rise to soluble aluminum salts. Mention has been made before that aluminum is present in the soil as oxide, hydrated oxides, hydroxides, phosphates and silicates. But which of these compounds breaks up so readily in the soil to form soluble salts that proved injurious to crops in some soils, as has been found by Abbott, Conner and Smalley, and Ruprecht and Morse? We naturally look upon hydroxides. There are three forms of aluminum hydroxides recognized: Diaspore— $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, bauxite— $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and gibbsite, otherwise called hydrar-gillite or oxyhydrates, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (53). Do these three forms behave chemically the same with mineral acids? Diaspore and bauxite are insoluble in cold and hot water and in acids and alkalies, but gibbsite, while not soluble in cold and hot water, is soluble in acid and alkalies (48). Moreover, the so-called aluminum salts, aluminum nitrate, $\text{Al}_2\text{O}_6(\text{NO}_2)_6$, aluminum acetate, $\text{Al}_2\text{O}_6(\text{C}_2\text{H}_5\text{O})_6$, aluminum sulfates, $\text{Al}_2\text{O}_6(\text{SO}_4)_3$, and aluminum phosphate $\text{Al}_2\text{O}_6(\text{PO}_4)_2$ —are chemically considered as derivatives of the oxyhydrates (53). Gibbsite, therefore, answers the first question, and the next question that comes up is, whether gibbsite is present in the soils of America.

Lateritization in northern climates. In the decomposition of rocks an insoluble residue made up mainly of silica, alumina and ferric oxide, and combined with water, is left over. When kaolinite is the predominant constituent of the residue it is called clay, but when hydrates of alumina and iron predominate the residue is called laterite. Hence, the process of rock decomposition in which kaolinite is the end product is called kaolinization and that process in which hydrates of alumina and limonite are the ultimate products is called lateritization (15). In regard to the latter process Clarke (12) says, "In the tropical and subtropical regions the processes of rock decay are often carried further than is usually the case within the temperate zones. The leaching is more complete, the silicates are more thoroughly decomposed, and the residues are richer in hydroxides."

There is a general opinion among geologists that kaolinization is characteristic of rock decomposition in northern climates while lateritization is characteristic of that in tropical and subtropical regions. For this reason there is a diversity of opinion as to the occurrence of aluminum hydrates in the soils of America. Cameron and Bell (11) for example, state that "either gibbsite or bauxite is but seldom found in soil," and that in the examination of several thousand soils from all over the United States, in only one soil, that which comes from southern California, was aluminum hydroxide observed. Lindgren (40) is also of the opinion that little or no aluminum hydroxide is formed in ordinary rock weathering, and that the occurrence of bauxite is a rarity in

the temperate climate. On the other hand, Edwards (15) by recalculating analytical data for clays from different states, shows that bauxite exists in 21 states besides those in which the mineral exists in deposits of commercial value. In regard to the independence of bauxite as a mineral species Lindgren (40) says, "The independence of bauxite as a mineral species, is, however, questioned and it is believed rather to be a mixture of diaspore and gibbsite. The Georgia bauxite according to T. L. Watson corresponds well to gibbsite." Hilgard (30) found a high ratio of alumina to soluble silica in some of the soils he examined, and could not attribute it to other than the presence of hydrous alumina, possibly gibbsite. Beyer and Williams (7) reporting the analyses of flint fire clays from Missouri and New Jersey, also found a higher ratio of alumina to silica than that found in kaolinite but attributed it to the presence of a more highly aluminous silicate which he called phalerite. In the reported analyses of ball and flint clays from Missouri and of fire clays from Pennsylvania, Rolfe (58), again, found a high proportion of alumina to silica, and attributed this to the presence in the clays of gibbsite or other minerals high in alumina. Ries (54) believes that there is the possibility that in kaolins high in aluminum bauxite or gibbsite might be present. Finally, Galpin (21) in the study of flint clays and their associates encountered highly aluminous fire clays from near St. Louis, Missouri, and proves that the excess of alumina to silica is due to the presence of gibbsite.

The author does not pretend to show that aluminum hydrates are of common occurrence in the soils in America, but with the evidence gathered from the works of the men mentioned above he can not help reaching the conclusion that in some soils in the United States hydrates of alumina are present, and that in the case of soils where sufficient amounts of soluble salts of aluminum are found to be harmful to crops, the aluminum compound furnishing the aluminum is gibbsite, and until further investigations prove the contrary the author will hold to this view.

IV. EXPERIMENTAL

The problem

The work reported in this paper has been undertaken with the view of gaining some information on the following questions:

1. Aluminum is found in the soil in abundance and in conditions of varying stability. When an acid soil is extracted with potassium nitrate solution aluminum is brought into solution and is largely responsible for the acid reaction of the extract. Is not the acidity of the so-called acid soil due to the presence of active aluminum in the soil?
2. Sweet clover does not grow on a strongly acid soil while other plants have their growth depressed. Since aluminum salts have been found highly toxic even in dilute solutions, is not this behavior a reaction to the toxicity of soluble salts of aluminum in the soil?

3. When acid soils are treated with limestone according to the potassium nitrate method, sweet clover thrives well. Does not calcium carbonate eliminate the toxicity of aluminum? And if so, how does it act?

4. Does acid phosphate increase the acidity of an acid soil?

5. If the acidity of the soil is due to the presence of active aluminum, what effects have soluble salts of aluminum on sweet clover grown in sand? What effect has aluminum salts on sweet clover in the presence of calcium carbonate, or acid phosphate?

General plan of the work

Based on the foregoing propositions, plans have been carried out:

1. To study the potassium nitrate extract of an acid soil before and after the application of limestone.
2. (a) To leach out a considerable quantity of acid soils with potassium nitrate and with water until the last 125 cc. of leachings no longer indicate acidity, and to grow crops on it.
(b) To analyze the leached out soils for aluminum, iron and manganese.
3. (a) To grow crops on acid soils, treated with limestone and acid phosphate, alone and in combination with each other, and in different amounts.
(b) To set aside a similar series as above, giving the same treatment except the growing of crops, for acidity determinations in two different periods.
4. To grow crops on sand treated with aluminum sulfate, aluminum chloride and aluminum nitrate and aluminum hydroxide, alone and in combination with calcium carbonate or with acid phosphate.

Description of the material used

Three types of soil have been secured from southern Illinois for this work. They are—gray silt loam, on tight clay of the lower Illinoian glaciation area; yellow gray silt loam, an upland timber soil; and yellow silt loam from the unglaciated areas. All the soils were acid to the blue litmus paper test. The physical composition of these soils is given in table 3. The Bureau of Soil's method and grades of mechanical separation have been adopted in this analysis (42). Some of the chemical constituents of the soils are given also in column 2, table 4. Except for aluminum, iron and manganese, the methods of chemical analysis used were those of the University of Illinois Agricultural Experiment Station. Aluminum, iron and manganese were determined by a combination of some of Hillebrand's procedures and of some in Treadwell's "Qualitative Analyses." The sample was fused with sodium bicarbonate, and the subsequent steps as directed in Hillebrand's methods, were followed up to the point of precipitating aluminum and iron. The ammonium persulfate method was adopted at this point to precipitate the manganese together with aluminum and iron (31). Manganese was then separated from aluminum and iron by the barium carbonate method and determined as manganese

pyrophosphate as directed in Treadwell's process (73). Aluminum was separated from iron by the potassium hydroxide procedure and both were weighed as oxides, also according to the direction of Treadwell.

Gray silt loam. This is a surface soil taken from the border of one of the control plots of the experimental fields at Newton, Jasper County. It contains 98.24 per cent dry matter. The reaction as tested in the laboratory is acid, and the acidity or lime requirements according to the Hopkins method is 2125 pounds of limestone of 93 per cent purity, per acre (2,000,000 pounds of soil $6\frac{2}{3}$ inches). The amounts of essential plant-food elements found are: nitrate-nitrogen 26 pounds per acre; total nitrogen 2900 pounds; phosphorus 1104 pounds; potassium 25,130 pounds; calcium 4510 pounds; magnesium 4520 pounds; and iron 47,800 pounds. Besides these the soil contains 840 pounds of manganese and 121,000 pounds of aluminum per acre.

TABLE 3
Physical analysis of the soil (grades of Bureau of Soils)

CONSTITUENTS	SIZE OF PARTICLES	GRAY SILT	YELLOW GRAY SILT	YELLOW SILT
		mm.	percent	percent
Moisture.....		1.76	1.36	1.61
Fine gravel.....	2-1*	0.93	1.37	0.00
Coarse sand.....	1.0 -0.5	2.15	1.79	0.21
Medium sand.....	0.5 -0.25	5.77	2.57	0.44
Fine sand.....	0.25-0.1	10.93	4.09	0.97
Very fine sand.....	0.1 -0.05	25.26	20.72	52.35
Silt.....	0.05-0.005	44.61	50.99	19.54
Clay (by difference).....	0.005	10.15	18.45	26.47
Total.....		99.80	99.99	99.98

* Calculated on water-free basis.

Yellow gray silt loam. This was taken from the farm of Joseph Quizzell at Carmi, White County, Illinois. It contains 98.64 per cent of dry matter. The reaction is acid and the lime requirements amount to 2814 pounds of limestone per acre. The essential plant-food elements found amount to 36 pounds of nitrate nitrogen per acre; 1370 pounds of total nitrogen; 693 pounds of phosphorus; 35,800 pounds of potassium; 3920 pounds of calcium; 4180 pounds of magnesium; and 74,200 pounds of iron. The manganese and aluminum found amount to 786 pounds and 151,000 pounds, respectively.

Yellow silt loam. This was taken near Vienna, Johnson County. It contains 98.39 per cent of dry matter. The reaction is acid and the lime requirement amounts to 2921 pounds per acre. The essential plant-food elements run up to 60 pounds of nitrate-nitrogen per acre; 1966 pounds of total nitrogen; 691 pounds of phosphorus; 29,000 pounds of potassium; 7850 pounds of calcium; 5330 pounds of magnesium and 74,200 pounds of iron. Manganese and aluminum reached 660 pounds and 14,900 pounds per acre, respectively.

TABLE 4
Gray silt loam

DETERMINED	ORIGINAL		EXTRACTED WITH KNO_3		EXTRACTED WITH H_2O	
	98.24 per cent		98.15 per cent		98.28 per cent	
	P.p.m. ¹	Pounds per acre ²	P.p.m.	Per cent extracted	P.p.m.	Per cent extracted
Acidity.....	988	2,125	30	96.96	925	7.31
Aluminum.....	60,500	121,000	33,400	44.79	49,800	17.67
Calcium.....	2,255	4,510	2,225	1.53	2,253	0.08
Iron.....	23,900	47,800	18,300	23.85	22,100	7.53
Magnesium.....	2,260	4,520	2,250	0.43	2,259	— ⁴
Manganese.....	420	840	400	4.76	415	1.19
Nitrate-nitrogen.....	13	26	29	22.69 ³	11	15.39
Nitrogen.....	1,450	2,900	1,451	— ⁴	1,450	— ⁴
Phosphorus.....	550	1,104	481	12.54	549	— ⁴
Potassium.....	12,560	25,130	40,140	28.95	12,420	1.11

Yellow gray silt loam

DETERMINED	ORIGINAL		EXTRACTED WITH KNO_3		EXTRACTED WITH H_2O	
	96.64 per cent		99.03 per cent		98.93 per cent	
	P.p.m.	Pounds per acre	P.p.m.	Per cent extracted	P.p.m.	Per cent extracted
Acidity.....	1,358	2,813	11	99.93	1,260	7.21
Aluminum.....	75,600	151,200	30,300	59.93	58,900	24.73
Calcium.....	1,960	3,920	1,950	0.51	1,958	— ⁴
Iron.....	20,100	40,300	16,700	14.44	19,600	2.48
Magnesium.....	2,095	4,180	2,090	— ⁴	2,090	— ⁴
Manganese.....	393	786	391	3.03	389	1.02
Nitrate-nitrogen.....	18	36	40	55.00 ³	15	16.66
Nitrogen.....	685	1,370	690	— ⁴	689	— ⁴
Phosphorus.....	336	693	275	18.15 ³	335	— ⁴
Potassium.....	17,900	35,800	24,100	25.72	17,880	0.11

Yellow silt loam

DETERMINED	ORIGINAL		EXTRACTED WITH KNO_3		EXTRACTED WITH H_2O	
	98.39 per cent		98.84 per cent		98.39 per cent	
	P.p.m.	Pounds per acre	P.p.m.	Per cent extracted	P.p.m.	Per cent extracted
Acidity.....	1,318	2,921	28	97.93	1,155	13.36
Aluminum.....	74,700	149,400	36,900	50.61	58,600	21.55
Calcium.....	3,425	7,850	3,400	0.72	3,410	0.43
Iron.....	37,100	74,200	2,930	21.01	33,900	8.62
Magnesium.....	2,665	5,330	2,660	— ⁴	2,664	— ⁴
Manganese.....	330	660	301	8.79	325	1.51
Nitrate-nitrogen.....	30	60	315	90.47 ³	23	23.33
Nitrogen.....	983	1,966	983	— ⁴	981	— ⁴
Phosphorus.....	346	691	292	15.61	339	2.02
Potassium.....	14,500	29,000	22,300	28.57 ³	14,400	0.69

¹ CaCO_3 .

² Limestone requirements 2,000,000 pounds of soil.

³ Increase.

⁴ Within the limits of probable error.

While a considerable amount of a calcium is present in these soils, qualitative tests for carbonates showed only traces, which indicate that these soils are deficient in calcium carbonate. It may be added further that while these soils are well provided with potassium, the phosphorus and nitrogen contents are rather low. On the other hand, the aluminum content is very high.

Sweet clover (biennial variety) was the crop used in this work for the reason that it does not thrive in strongly acid soils, and will, therefore, respond more readily to soil treatment. Inoculated seeds were used in every case.

The experiments were carried out in 1-gallon pots, each holding about 5 kgm. (11 pounds) of soil.

Experiment I. Effect of aluminum salts, alone and in combination with calcium carbonate or with acid phosphate on sweet clover grown in sand

Three salts, aluminum sulfate, aluminum chloride and aluminum nitrate, and one hydroxide, aluminum monohydroxide, were used. When applied alone the chemicals were used in three different amounts, one, for the sake of convenience, is called normal application, the second, one-fifth the normal, and the third, five times the normal application. The basis for the normal application is the acidity or lime requirement of the yellow silt loam, which is 2921 pounds limestone per acre, or 6.79 gm. calcium carbonate per 5 kgm. of soil. In other words, the normal application is the chemical equivalent of the salts to 6.79 gm. of calcium carbonate. In combination with calcium carbonate or with acid phosphate the salts remained constant while calcium carbonate and acid phosphate were applied in three different amounts, normal, one-fifth normal and five times normal. The normal application of calcium carbonate is the lime requirement of the soil and that of acid phosphate the chemical equivalent to the normal application of the salts. For the sake of brevity, hereafter throughout the discussion, we will refer to these three different amounts as the normal, the minimum, and the maximum application.

The chemicals were thoroughly incorporated in the sand, and seeds of sweet clover were sown. In order to insure a sufficient number of good seedlings the seeds were sown rather freely, but as the plants grew they were gradually thinned out until finally only five plants were left in each pot. The plant-food solutions were prepared and applied as directed in Hopkins and Pettit's "Soil Fertility Laboratory Manual" (34). Two crops have been grown in this series. The first was planted on July 17 and harvested November 1, 1919; the second was planted on January 19, but because of some unknown causes the seedlings failed to attain a uniform stand, so the whole series was replanted on February 2. The crop was harvested on May 21. The yields for two crops are given in table 5.

During the first crop several things were observed which led up immediately to the setting up of another series, and to the introduction of some modifications in the treatment of the pots for the second crop. In the first place, it was noticed that on every pot receiving acid phosphate no plant would grow.

Since the application of acid phosphate was rather heavy, 964 pounds to the acre or 5.3 gm. per pot, it was thought that the failure of the plants to grow might have been due to excessive amounts of acid phosphate present rather than to the presence of aluminum; accordingly a new series with acid phosphate alone, and in combination with calcium carbonate, was set up. This was designated as 600 series. The results of this series are shown in plate 6. It proved the supposition true that acid phosphate in such amounts was injurious to seedlings. Even calcium carbonate in amounts sufficient to neutralize the acidity of the acid phosphate did not prevent the harmful effect of acid phosphate. With this experience the application of acid phosphate was reduced to from 100 to 400 pounds to the acre, in the second planting.

TABLE 5
Aluminum series (dry weight of five plants)

SERIES NUMBER	FIRST CROP ¹		SERIES NUMBER	FIRST CROP		SERIES NUMBER	FIRST CROP		SERIES NUMBER	FIRST CROP		SERIES NUMBER	FIRST CROP	
	gm.	gm.		gm.	gm.		gm.	gm.		gm.	gm.		gm.	gm.
101	3.40 ²	9.73	201	4.10	301	3.50	8.89	401	9.13	11.11	411	8.51		
102	0.00	3.60	202	0.00	302	0.00	1.85	402	8.74	14.07	412	10.42		
103	2.85	8.20	203	0.00	303	1.40	8.02	403	10.80	12.29	413	0.00		
104	0.00	0.00	204	0.00	304	0.00	0.00	404	3.67	12.14	414	7.14		
105	16.59	13.06	205	17.15	305	11.99	11.68	405	15.41	13.24	415	9.16		
106	1.65	5.50	206	0.80	306	4.22	5.38	406	13.13	11.38	416	14.87		
107	18.52	10.04	207	16.07	307	16.17	19.73	407	9.36	9.74	417	14.03		
108	0.00	2.72	208	0.00	308	0.00	2.55	408	0.00	10.56	418	0.00		
109	0.85	2.02	209	0.00	309	4.00	1.93	409	20.00	11.68	419	9.72		
110	0.00	4.07	210	0.00	310	0.00	6.56	410	0.00	14.50				

¹ Harvested at the age of 106 days.

² Average of 2 pots.

³ Harvested at the age of 108 days.

The second observation made was on the showing of the plants in the control pots of every series, except those of the aluminum monohydroxide series. The plants in these pots appeared to be suffering from lack of some elements. Since the plant-food solution applied to the pots did not contain calcium, it was thought that the plants in the controls might have been suffering from lack of calcium, in which case the results of the different treatments would not be comparable. Following this thought it was planned for the second crop to apply calcium silicate to each pot as a source of calcium, and in quantities having calcium equal to the amount contained in calcium carbonate applied as normal.

The third observation made was on the aluminum monohydroxide series in which all pots except those receiving the maximum amount of aluminum monohydroxide, and acid phosphate, show no effect of the presence of aluminum.

This compound, being insoluble, will produce no toxic effect, but it was thought that adding some substances which would yield acids on decomposition might change the aluminum hydroxide into a soluble form of aluminum, thus throwing further light on the form of aluminum compounds in the soil that produce toxicity. So it was planned for the next crop to introduce ammonium sulfate and dried blood in the series. Then the aluminum chloride series was dropped out in order to give way to this plan. Following is the plan of the experiments. Every treatment was carried out in duplicate.

PLAN OF THE EXPERIMENT

100 Series—Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$

7.75 gm., or 3100 lbs. to the acre $\text{Al}_2(\text{SO}_4)_3 = 6.79$ gm. CaCO_3

5.3 gm., or 964 lbs. to the acre $\text{CaH}_4(\text{PO}_4)_2 = 7.75$ gm. $\text{Al}_2(\text{SO}_4)_3$ according to the following equation:



101. Control—Plant-food only
102. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$
103. Plant-food + $\frac{1}{2}$, or 1.55 gm. $\text{Al}_2(\text{SO}_4)_3$
104. Plant-food + 5×7.75 gm., or 38.75 gm. $\text{Al}_2(\text{SO}_4)_3$
105. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3 + 6.79$ gm. CaCO_3
106. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3 + \frac{1}{2}$, or 0.36 gm. CaCO_3
107. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3 + 5 \times$, or 33.95 gm. CaCO_3
108. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3 + 5.3$ gm. $\text{CaH}_4(\text{PO}_4)_2$
109. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3 + \frac{1}{2}$, or 1.06 gm. $\text{CaH}_4(\text{PO}_4)_2$
110. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3 + 5 \times$, or 26.5 gm. $\text{CaH}_4(\text{PO}_4)_2$

200 Series—Aluminum chloride, AlCl_3

6.04, or 2405 pounds to the acre $\text{AlCl}_3 = 6.79$ gm. CaCO_3

5.3 gm., or 964 pounds to the acre $\text{CaH}_4(\text{PO}_4)_2 = 6.04$ gm. AlCl_3 according to the following equation:

$$2\text{AlCl}_3 + \text{CaH}_4(\text{PO}_4)_2 = 2\text{AlPO}_4 + \text{CaCl}_2 + 4\text{HCl}$$

201. Control—Plant-food only
202. Plant-food + 6.04 gm. AlCl_3
203. Plant-food + $\frac{1}{2}$, or 1.21 gm. AlCl_3
204. Plant-food + $5 \times$, or 30.2 gm. AlCl_3
205. Plant-food + 6.04 gm. $\text{AlCl}_3 + 6.79$ gm. CaCO_3
206. Plant-food + 6.04 gm. $\text{AlCl}_3 + \frac{1}{2}$, or 1.36 gm. CaCO_3
207. Plant-food + 6.04 gm. $\text{AlCl}_3 + 5 \times$, or 33.95 gm. CaCO_3
208. Plant-food + 6.04 gm. $\text{AlCl}_3 + 5.3$ gm. $\text{CaH}_4(\text{PO}_4)_2$ CaCO_3
209. Plant-food + 6.04 gm. $\text{AlCl}_3 + \frac{1}{2}$, or 1.06 gm. $\text{CaH}_4(\text{PO}_4)_2$ CaCO_3
210. Plant-food + 6.04 gm. $\text{AlCl}_3 + 5 \times$, or 26.5 gm. $\text{CaH}_4(\text{PO}_4)_2$ CaCO_3

300 Series—Aluminum nitrate, $\text{Al}(\text{NO}_3)_3$

9.65 gm., or 3859 pounds to the acre $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \times 6.79$ gm. CaCO_3

5.3 gm., or 964 pounds to the acre $\text{CaH}_4(\text{PO}_4)_2 = 9.65$ gm. $\text{Al}(\text{NO}_3)_3$ according to the following equation:

$$2\text{Al}(\text{NO}_3)_3 + \text{CaH}_4(\text{PO}_4)_2 = 2\text{AlPO}_4 + \text{CaNO}_3 + 4\text{HNO}_3$$

301. Control—Plant-food only
302. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$
303. Plant-food + $\frac{1}{2}$, or 1.93 gm. $\text{Al}(\text{NO}_3)_3$

304. Plant-food + 5 X, or 46.25 gm. Al(NO₃)₃
305. Plant-food + 9.65 gm. Al(NO₃)₃ + 6.79 gm. CaCO₃
306. Plant-food + 9.65 gm. Al(NO₃)₃ + $\frac{1}{2}$, or 1.36 gm. CaCO₃
307. Plant-food + 9.65 gm. Al(NO₃)₃ + 5 X, or 33.95 gm. CaCO₃
308. Plant-food + 9.65 gm. Al(NO₃)₃ + 5.3 gm. CaH₄(PO₄)₂
309. Plant-food + 9.65 gm. Al(NO₃)₃ + $\frac{1}{2}$, or 1.06 gm. CaH₄(PO₄)₂
310. Plant-food + 9.65 gm. Al(NO₃)₃ + 5 X, or 26.5 gm. CaH₄(PO₄)₂

400 Series—Aluminum Hydroxide, Al(OH)₃

3.5 gm., or 1399 pounds to the acre Al(OH)₃ = 6.79 gm. CaCO₃
 7.8 gm. CaH₄(PO₄)₂, or 1418.5 pounds per acre, or 3.5 gm. Al(OH)₃ according to the following equation:

$$4 \text{ Al(OH)}_3 + 3 \text{ CaH}_4(\text{PO}_4)_2 = 4 \text{ AlPO}_4 + \text{Ca}_3(\text{PO}_4)_2 + 12 \text{ H}_2\text{O}$$

401. Control-Plant-food only
402. Plant-food + 3.5 gm. Al(OH)₃
403. Plant-food + $\frac{1}{2}$, or 0.7 gm. Al(OH)₃
404. Plant-food + 5 X, or 17.5 gm. Al(OH)₃
405. Plant-food + 3.5 gm. Al(OH)₃ + 6.79 gm. CaCO₃
406. Plant-food + 3.5 gm. Al(OH)₃ + $\frac{1}{2}$, or 1.36 gm. CaCO₃
407. Plant-food + 3.5 gm. Al(OH)₃ + 5 X, or 33.95 gm. CaCO₃
408. Plant-food + 3.5 gm. Al(OH)₃ + 7.8 gm. CaH₄(PO₄)₂
409. Plant-food + 3.5 gm. Al(OH)₃ + $\frac{1}{2}$, or 1.5 gm. CaH₄(PO₄)₂
410. Plant-food + 3.5 gm. Al(OH)₃ + 5 X, or 39.0 gm. CaH₄(PO₄)₂

600 Series—Acid phosphate, CaH₄(PO₄)₂

601. Control—Plant-food only
602. Plant-food + 5.3 gm. CaH₄(PO₄)₂
603. Plant-food + $\frac{1}{2}$, or 1.06 gm. CaH₄(PO₄)₂
604. Plant-food + 5 X, or 26.5 gm. CaH₄(PO₄)₂
605. Plant-food + 5.3 gm. CaH₄(PO₄)₂ + 6.79 gm. CaCO₃
606. Plant-food + 5.3 gm. CaH₄(PO₄)₂ + $\frac{1}{2}$, or 1.36 gm. CaCO₃
607. Plant-food + 5.3 gm. CaH₄(PO₄)₂ + 5 X, or 33.95 gm. CaCO₃

PLAN FOR SECOND CROP

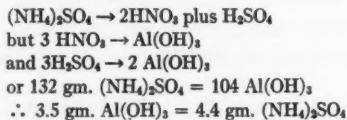
100 Series. The same as before with the addition of 7.9 gm. CaSiO₃ to each pot and the reduction of the acid phosphate application to from 100 to 400 pounds to the acre, or from 350 mgm. to 1.00 gm. per pot.

300 Series. The same plan as before with the same modification noted in the 100 series.

400 Series. Up to 410, inclusive, the same plan as before with the same modification as noted in the 100 series.

From 411 to 424 the following arrangement has been followed:

From 411 to 417, inclusive, 4.4 gm. (NH₄)₂SO₄ has been added according to the following reaction:



From 418 to 424, inclusive, 13.33 gm. of dried blood has been added, according to the following reaction. The dried blood used contained 14 per cent N, or 17 gm. NH₄.

If all ammonia produced is nitrified, 2 HNO₃ is produced.

But HNO₃ = Al(OH)₃

∴ 189 gm. HNO₃ = 78 gm. Al(OH)₃

3.5 gm. Al(OH)₃ = 8.4 gm. HNO₃, or 13.33 gm. dried blood

411. Plant-food + 3.5 gm. Al(OH)₃ + 4.4 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
412. Plant-food + 3.5 gm. Al(OH)₃ + $\frac{1}{2}$, or 0.88 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
413. Plant-food + 3.5 gm. Al(OH)₃ + 5 \times , or 0.22 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
414. Plant-food + 17.5 gm. Al(OH)₃ + 4.4 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
415. Plant-food + 3.5 gm. Al(OH)₃ + 4.4 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
416. Plant-food + 3.5 gm. Al(OH)₃ + 4.4 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
417. Plant-food + 3.5 gm. Al(OH)₃ + 4.4 gm. (NH₄)₂SO₄ + 7.9 gm. CaSiO₃
418. Plant-food + 3.5 gm. Al(OH)₃ + 13.33 gm. dried blood
419. Plant-food + 3.5 gm. Al(OH)₃ + $\frac{1}{2}$, or 2.66 gm. dried blood
420. Plant-food + 3.5 gm. Al(OH)₃ + 5 \times , or 66.65 gm. dried blood
421. Plant-food + 17.5 gm. Al(OH)₃ + 13.33 gm. dried blood
422. Plant-food + 3.5 gm. Al(OH)₃ + 13.33 gm. dried blood
423. Plant-food + 3.5 gm. Al(OH)₃ + 13.33 gm. dried blood
424. Plant-food + 3.5 gm. Al(OH)₃ + 13.33 gm. dried blood

Results and discussion. The effect of aluminum salts, of aluminum hydroxide and of acid phosphate on the growth of sweet clover, is best shown in the photographs in plates 2, 3, 4, 5 and 6.

In the first crop in which no compound as a source of calcium was applied to the pots, aluminum sulfate proved to be injurious to sweet clover even in very small amounts. This may be seen in pots 102, 103 and 104 in which aluminum sulfate alone was applied. In pot 104, which received the maximum application of the salt, absolutely no seed could germinate. Pot 106, receiving the normal application of aluminum sulfate and one-fifth the normal application of calcium carbonate, shows that in small amounts calcium carbonate cannot correct the toxic effect of aluminum. On the other hand, where calcium carbonate has been applied in larger amounts, normal and maximum, sweet clover exhibited enormous growth. In the case of pots receiving aluminum sulfate and acid phosphate, those receiving 964 pounds and 4820 pounds of acid phosphate per acre failed to grow any crop.

What has been said about the effect of aluminum sulfate on sweet clover can also be said for aluminum chloride and aluminum nitrate. But with aluminum hydroxide the result is different. The normal application of aluminum hydroxide did not have any effect on sweet clover; the maximum, however, caused some depression. It is also important to note that whereas in the combination of aluminum salts and the minimum acid phosphate application, no sweet clover grew, but in that of the aluminum hydroxide and minimum acid phosphate no effect was shown. This proves that the failure of sweet clover to grow in pots 109, 209 and 309 was due to the presence of aluminum rather than that of acid phosphate.

The results of the second cropping, in which calcium silicate was added as a source of calcium, and the application of acid phosphate has been reduced to from 100 to 400 pounds per acre, were different from those of the first crop.

First, the normal application of aluminum sulfate did not show any toxic effect at all, while the maximum application was always fatal to sweet clover. Second, in every case where calcium carbonate was applied, no matter in what amount, good plants were growing, indicating that active aluminum has been put out of action. Acid phosphate in decreased amounts seemed to help in reducing the injurious effect of aluminum sulfate.

The results with aluminum nitrate were different from those noted in the case of sulfate. The normal application showed very toxic effects. While the maximum application of calcium carbonate was beneficial to clover the normal application did not entirely eliminate the toxicity of aluminum nitrate. The action of acid phosphate in eliminating the toxicity of aluminum nitrate was much less pronounced than in the case of the sulfate. From this difference of the behaviour of sweet clover on the two salts we are led to conclude that aluminum nitrate chemically equivalent to the acidity of the soil is more toxic than aluminum sulfate.

In the case of aluminum hydroxide, up to pot 419 with the exception of pots 413 and 419, the stand of sweet clover was uniform. Even the maximum application did not produce any effect on the growth of the plants. Pot 413 received 22 gm., the maximum application, of ammonium sulfate. The fact that sweet clover did not grow cannot be attributed to any cause but to an excessive amount of ammonium salt which, on breaking down, liberates ammonia that causes injury to the germinating seeds. Pot 418 received 13.33 gm., the normal application, of dried blood. Pot 419 received 2.66 gm., the minimum application, of dried blood. And the fact that on the former nothing grew, while on the latter the crop was as good as that in any other pot in the series, can be attributed also to the excessive amount of dried blood which on decomposition produces ammonia that hinders the germination of seeds. Apparently neither ammonium sulfate nor dried blood in smaller amounts was able to change aluminum hydroxide into other forms of aluminum which could produce the same effect as aluminum sulfate or nitrate.

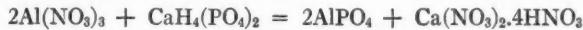
The effect of aluminum salts on sweet clover in the presence of calcium carbonate. In the series with aluminum sulfate, chloride and nitrate we have noted that in the presence of an excess of calcium carbonate the toxicity of the salts was overcome. Ruprecht and Morse (60) found this to be true also in their water-culture investigation with aluminum and iron sulfates in which, whenever calcium carbonate was added in excess to the solution containing aluminum and iron, the toxicity of these metals has been eliminated and good healthy plants grew in the solution. With this fact the question naturally arises as to what became of the aluminum. The most logical conclusion would be that aluminum had entered into combination with other elements forming an insoluble compound. Ruprecht and Morse (60) suggested that aluminum was precipitated as hydroxide and as such had no effect on the plants grown in the solution. The results of the test carried out in this work proved that aluminum monohydroxide has no effect on sweet clover. But whether the

hydroxide precipitated by the introduction of calcium carbonate is the variety that does not dissolve in water, acid and alkali, the author seriously doubts. In fact, he is of the opinion that the aluminum hydroxide precipitated by the introduction of calcium carbonate is like that formed when ammonia and sodium or potassium hydroxide is added to a solution containing aluminum. This is aluminum trihydroxide, which is insoluble in water and would therefore have no effect on the plants grown in solution. But this form of hydroxide is soluble even in dilute acids (53), and in sand or soil where chemical changes are constantly taking place this form of aluminum hydroxide will not remain long, for it will be converted into aluminum sulfate, chloride and nitrate as fast as free sulfuric, hydrochloric and nitric acids are produced in the soil and as long as the soil is not supplied with calcium or other suitable bases. For this reason the author looks into the formation of a more stable aluminum compound as an explanation for the elimination of active aluminum when calcium carbonate is added to sand or soil. He is of the opinion that as soon as calcium bicarbonate is formed by the action of carbonated water on calcium carbonate, the bicarbonate reacts with the aluminum salts forming calcium aluminate. The reaction may be written as follows:



Calcium aluminate is one of the constituents of portland cement and is a very stable compound. The formation of this compound seems to be the only satisfactory explanation for the ineffectiveness of aluminum as a toxic substance in the presence of sufficient calcium carbonate.

The effect of aluminum salts on sweet clover in the presence of acid phosphate. Mention has been made before that the 964 pounds per acre application of acid phosphate proved to be detrimental to sweet clover, and that the failure of the crop in the pots which received the normal and maximum application was brought about by the excess of acid phosphate. But in the second crop where the acid phosphate was applied in reduced amounts from 100 to 400 pounds per acre, the results showed that acid phosphate reduced the toxicity of aluminum. While the pots receiving the minimum and normal application in series 300 did not show any reduction of the toxicity of aluminum nitrate, the reduction of toxicity in the pot receiving 400 pounds of acid phosphate per acre is very pronounced, as indicated by the fairly good growth of the plants. Evidently the minimum and normal applications were not sufficient to convert the larger portion of aluminum into an insoluble form. Now the question arises as to how acid phosphate reduced the toxicity of aluminum. The answer is that with acid phosphate, aluminum sulfate, chloride and nitrate form an insoluble compound. In this case the compound is aluminum phosphate and is formed according to the following reaction:



Under soil conditions this reaction is probably never complete; nevertheless, a great amount of insoluble aluminum phosphate is formed. But the free nitric acid formed might also react with more aluminum, thus repeating the process until equilibrium is finally reached. Aluminum phosphate is highly insoluble and Wheeler (82) thinks that in the case of acid soils it is desirable to apply lime before or at the same time with acid phosphate in order to prevent formation of aluminum phosphate which is even more insoluble than tricalcium phosphate.

Experiment II. Effect of limestone and acid phosphate alone and in combination on the productivity and acidity of acid soils

Ten duplicate pots for each type of soil were filled with about 5 kgm. (11 pounds) of soil, and treated according to the following plan:

PLAN OF THE EXPERIMENT

700 Series—Gray silt loam

Acidity = 4.94 gm. CaCO_3 per 5 kgm., or 5.3 gm. limestone of 93 per cent purity, or 2125 pounds to the acre.

701. Control (nothing)
702. Soil + 5.3 gm. limestone
703. Soil + $\frac{1}{2}$, or 1.0 gm. limestone
704. Soil + 5 \times , or 26.5 gm. limestone
705. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 1.05 tons to the acre
706. Soil + $\frac{1}{2}$, or 1.16 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 0.21 tons to the acre
707. Soil + 5 \times , or 29 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 5.25 tons to the acre
708. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 5.3 gm. limestone
709. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = $\frac{1}{2}$, or 1.06 gm. limestone
710. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 5 \times , or 26.5 gm. limestone

800 Series—Yellow gray silt loam

Acidity = 6.5 gm. CaCO_3 per 5 kgm., or 2813 pounds limestone to the acre

801. Control
802. Soil + 7.03 gm. limestone
803. Soil + $\frac{1}{2}$, or 1.40 gm. limestone
804. Soil + 5 \times , or 35.15 gm. limestone
805. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 1.4 tons to the acre
806. Soil + $\frac{1}{2}$, or 1.5 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 0.28 tons to the acre
807. Soil + 5 \times , or 38.0 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 6.00 tons to the acre
808. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 7.03 gm. limestone
809. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ + $\frac{1}{2}$, or 1.40 gm. limestone
810. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 5 \times , or 35.15 gm. limestone

900 Series—Yellow silt loam

Acidity + 6.79 gm. CaCO_3 per kgm., or 7.4 gm. limestone, or 2921 pounds limestone to the acre.

901. Control.
902. Soil + 7.3 gm. limestone
903. Soil + $\frac{1}{2}$, or 1.46 gm. limestone

904. Soil + 5 X, or 36.5 gm. limestone
 905. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 1.4 tons to the acre
 906. Soil + $\frac{1}{2}$, or 1.58 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 0.28 tons to the acre
 907. Soil + 5 X, or 39 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 6.00 tons to the acre
 908. Soil + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 7.3 gm. limestone
 909. Soil + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ + $\frac{1}{2}$, or 1.46 gm. limestone
 910. Soil + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 5 X, or 36.5 gm. limestone

Two crops have been harvested in these series. The first was planted on August 22, 1919, and harvested November 30, 1919, a period of only 100 days. The time of cropping could have been prolonged, but when the crop was moved into the greenhouse, the red spider infested it so badly that it was thought best to cut the crop down in order to eradicate the red spider at once. The second crop was planted on January 16, 1920, and harvested May 21, 1920, after a period of 125 days. The yield of the crops is given in table 6.

TABLE 6
Soil series (dry weight of five plants)

GRAY SILT			YELLOW GRAY SILT			YELLOW SILT		
Series number	First crop ¹	Second crop ²	Series number	First crop	Second crop	Series number	First crop	Second crop
	gm.	gm.		gm.	gm.		gm.	gm.
701	0.54 ²	2.02	801	0.27	0.40	901	0.52	0.79
702	0.81	2.77	802	0.68	2.29	902	0.64	1.26
703	0.70	2.07	803	0.26	0.26	903	0.52	1.29
704	1.28	5.35	804	0.97	3.45	904	1.41	2.11
705	0.87	2.20	805	0.40	0.60	905	0.75	4.72
706	0.58	1.62	806	0.23	1.68	906	0.62	1.38
707	1.12	3.18	807	0.67	1.48	907	1.21	1.45
708	1.65	5.88	808	0.71	10.58	908	1.19	4.67
709	0.76	1.58	809	0.34	1.80	909	0.71	1.10
710	1.43	7.42	810	1.45	14.67	910	1.66	6.49

¹ Harvested at the age of 106 days.

² Average of 2 pots.

³ Harvested at the age of 108 days.

For each type of soil a corresponding set of treated pots was laid aside, without plants for acidity determination. Two determinations were made, the first on December 8, 1919, after a lapse of 108 days from the time the pots were set aside, and the second on February 16, 1920, a period of 70 days after the first determination. Table 7 shows the results of these determinations.

Results and discussion. The effect of lime and acid phosphate on sweet clover grown on acid soils can best be seen in the photographs in plates 6, 7, and 8. It can be seen that all the three types of soil respond to liming. The normal and maximum applications especially brought excellent results. The plants were healthy, vigorous and dark green. Limestone applied in amounts equal to one-fifth of the lime requirement did not benefit the soil at all. The growth of the plants in this case was comparable to that of the control in which

TABLE 7
Acidity determinations of treated soils

SERIES NUMBER	SAMPLED DECEMBER 8, 1919				SAMPLED FEBRUARY 16, 1920			
	P.p.m.	Acidity reduced after 108 days	Acidity above or below control	Acidity reduced due to treatment	P.p.m.	Acidity reduced after 178 days	Acidity above or below control	Acidity reduced between dates of sampling

Gray silt loam. Original acidity—988 parts per million, or 2125 pounds of limestone per acre

		per cent	per cent	per cent		per cent	per cent	per cent	per cent
701	705	28.66			685	30.87			2.83
702	165	83.29	76.59	54.63	74	92.51	89.19	55.15	62.64
703	640	35.22	9.22	6.56	425	56.98	37.95	33.59	26.11
704	26	97.26	96.31	68.60	Alkaline	100.00	0.00	0.00	
705	545	44.83	22.69	16.17	217	78.03	68.32	41.83	47.16
706	810	18.01	12.96		687	30.46	0.29	15.18	
707	467	52.85	33.75	24.19	115	88.35	83.19	75.37	57.48
708	106	89.27	84.96	60.61	Alkaline	100.00	0.00	0.00	
709	437	56.78	38.96	21.12	243	75.40	64.52	44.39	44.53
710	20	97.97	96.32	69.31	Alkaline	100.00	0.00	0.00	

Yellow gray silt loam. Original acidity—1358 parts per million, or 2813 pounds of limestone per acre

801	1066	21.63			970	28.57		9.00	
802	42	96.90	96.06	75.27	Alkaline	100.00	0.00	0.00	
803	542	60.09	49.06	38.46	362	73.34	61.64	33.21	44.7
804	Alkaline	100.00	0.00		Alkaline	0.00	0.00	0.00	
805	764	43.00	28.33	21.37	580	57.29	40.20	24.08	28.62
806	895	33.28	16.04	11.65	894	34.16	7.83	0.11	5.59
807	479	63.91	55.09	42.28	271	80.04	72.06	41.33	51.47
808	110	91.91	90.62	70.28	Alkaline	100.00	0.00	0.00	
809	565	65.75	46.43	44.12	519	61.78	46.49	8.01	33.21
810	Alkaline	100.00	0.00	0.00	Alkaline	100.00	0.00	0.00	

Yellow silt loam. Original acidity—1318 parts per million, or 2921 pounds of limestone per acre

901	685	48.02			683	48.18		0.29	
902	77	94.16	88.76	46.13	13	99.01	98.09	83.11	50.83
903	511	61.22	25.40	13.20	243	81.56	64.42	52.44	33.38
904	Alkaline	0.00	0.00		Alkaline	0.00	0.00	0.00	
905	630	52.20	8.26	4.18	441	65.78	35.43	30.00	17.60
906	832	36.71	17.66		645	51.06	5.56	22.47	2.88
907	455	65.47	33.57	17.45	123	90.66	81.99	72.96	52.48
908	109	91.72	84.09	43.70	Alkaline	100.00	0.00	0.00	0.00
909	846	35.81	19.05		642	51.29	6.00	24.11	3.11
910	16	98.78	96.21	50.76	Alkaline	100.00	0.00	0.00	

the plants were very small and chlorotic. The results with acid phosphate applied alone, showed that the soils also respond to phosphate fertilization. Judging from the growth of the plants even the minimum application seems to have benefited the soil. In the first crop, however, the plants looked different from those growing on limed pots. The plants grew more than those in the control, but they were slender, branchless, and chlorotic as compared with the bushy dark green plants growing on the limed pots. In the second crop, excepting the crops in the pots which received the minimum application, those defects observed above have disappeared, and although growth was slow during the winter days, the plants were healthy, bushy and deep green. The best crop in this series was noted in the pots receiving the normal application and maximum application of limestone, together with the normal application of acid phosphate. Even the minimum application of limestone in combination with the normal amount of acid phosphate grew better crops than the normal application of limestone alone. In the first crop, however, the plants were also chlorotic, although to a lesser extent than those in pots receiving acid phosphate alone. In the second crop chlorosis has completely disappeared.

After the first acidity determination it was found that the acidity of the untreated soil has been reduced also. The acidity of the gray silt loam has been reduced 28 per cent, that of the yellow gray silt $21\frac{1}{2}$ per cent and that of the yellow silt 48 per cent. Up to this time, for a period of 108 days, tap-water was used for watering the plants and the pots, but since then rain-water was used instead. Experience in the use of this tap-water in the greenhouse proved that it has a tendency to reduce the acidity of acid soils. For example, a very acid soil watered by the tap-water became alkaline after a few years. The fact that the acidity of the controls of the three types of soil have been reduced is attributed to the use of the tap-water. But by subtracting the per cent of acidity reduced in the control from the total acidity of the treated pots, we still have a fair indication of the acidity reduced due to the treatment of the soils.

The effect of limestone and acid phosphate alone and in combination on the acidity of the three acid soils is best shown in plates 11 and 12, in which the treatment of the pots is represented by the abscissas and the per cent of acidity reduced by the ordinates. Curve 1 in each figure represents the per cent of acidity reduced after 108 days and curve 2 the total acidity reduced for a period of 178 days.

The three types of soil responded differently to the different treatments. Of the three the yellow gray silt loam responded more readily to liming and phosphate fertilization than either of the other two types. From the charts we can see that in 108 days the normal application of limestone or the amount required to neutralize the acidity of the soil reduced the acidity of the gray silt about 55 per cent, of the yellow silt 46 per cent and that of the yellow gray silt 76 per cent. In 178 days the total acidity reduced was 63 per cent for the gray silt and 51 per cent for the yellow silt; the yellow gray silt was com-

pletely neutralized, the reaction being alkaline. With one-fifth of the normal application the acidity was reduced 6.56 per cent in the case of gray silt, in 108 days; 38 per cent in case of the yellow gray, and 13 per cent in case of the yellow silt. At the end of 178 days the lime applied was completely used up in the neutralization of one-fifth of the acidity of the soil. In the case of the yellow gray silt the percentage of acidity reduced in both determinations exceeds that which would theoretically be accomplished by lime applied in an amount equal to one-fifth of the lime requirement. This fact is probably due to experimental error which would include sampling and manipulation. When limestone equal to five times the lime requirement was added, the neutralization of acidity was complete in 108 days in the case of two soils; only 68.8 per cent of the acidity was reduced in the case of gray silt. All these facts indicate the rapidity with which calcium carbonate puts active aluminum out of action, the substance responsible for the acidity of the soils.

The effect of acid phosphate on the three soils is interesting. The notion that acid phosphate has the tendency to increase the acidity of a soil has no confirmation in this work. On the contrary, the results show that acid phosphate decidedly reduced the acidity of the soil, as measured by the Hopkins method. The reaction, however, is slower than that in the case of calcium carbonate. In 108 days the normal application of acid phosphate destroyed 16 per cent of the acidity of the gray silt; 21 per cent of that of the yellow gray silt; and 4 per cent of that of the yellow silt. At the end of 178 days 47 per cent of the acidity of the gray silt was destroyed; 28 per cent of that of the yellow gray silt and only 17 per cent of that of the yellow silt. Applied in one-fifth the normal application, acid phosphate reduced in 178 days the acidity of the gray silt 7 per cent; of the yellow gray silt 12 per cent; and of the yellow silt only 3 per cent. In five times the normal application acid phosphate reduced the acidity of the gray silt 24 per cent in 108 days and 57 per cent in 178 days; of the yellow gray silt 42 per cent in 108 days and 51 per cent in 178 days; of the yellow silt 17 per cent in 108 days and 52 per cent in 178 days.

The combination of acid phosphate and limestone produced a still more interesting result. The combination of the normal application of limestone and acid phosphate reduced, in 108 days the acidity of the gray silt 60 per cent; of the yellow gray silt 70 per cent; and of the yellow silt 43 per cent. After 178 days all the pots with this treatment were alkaline. The combination of the normal application of acid phosphate and one-fifth the normal dose of limestone also reduced considerably the acidity of the soils. But with the combination of the normal application of acid phosphate and the maximum of limestone, the yellow gray silt was alkaline in 108 days, while the gray and yellow silt were then reduced 69.31 per cent and 50.76 per cent, respectively. At the end of 178 days the soils were alkaline.

How acid phosphate reduces the acidity of acid soils. One of the problems in the present investigation is whether acid phosphate increases the acidity of an acid soil. Using the calcium-acetate method Hartwell and Pember (27) found

that the acidity of acid soils increases as the amount of acid phosphate applied was increased. Comparing the lime-water and the potassium-nitrate methods Albrecht¹ found also that with the lime-water method the acidity increased as the amount of acid phosphate was increased, but with the potassium-nitrate method up to a certain point, the increase of acid phosphate was accompanied by a decrease of acidity. The results discussed in the preceding paragraph corroborate the findings of Albrecht with the potassium-nitrate method. In this connection two questions come up. First, if acid phosphate reduced the acidity of the soil, how? And second, why are the results between the potassium-nitrate method on the one hand, and those of calcium-acetate and lime-water on the other, so diametrically opposed?

Hartwell and Pember (27) noted that while the acidity of the soils was increased with the increase of acid phosphate application the amount of active aluminum was decreased. No explanation was offered for this fact, but we can safely attribute it to the combination of active aluminum with other elements forming an insoluble compound. One of the products of the reaction between acid phosphate and active aluminum in the soil is aluminum phosphate, a very insoluble compound. The decrease in the amount of active aluminum after acid phosphate has been applied to the soil is, therefore, due to the formation of aluminum phosphate. The larger the amount of acid phosphate applied to the soil containing active aluminum, the larger will be the amount of aluminum phosphate formed. And since aluminum is largely responsible for the acid reaction of the potassium nitrate extract, the larger the amount of aluminum converted into phosphate, the smaller will be the amount of aluminum that will be brought into solution when an acid soil is extracted with potassium nitrate after acid phosphate has been applied. This explains the fact that with the potassium-nitrate method the acidity of acid soils decreases as the amount of acid phosphate applied increases.

We can see from the above explanation that the opposing results obtained by the use of the three methods of determining the acidity of the soil are due to the difference of the substances determined. The lime-water and calcium-acetate methods determine true acidity, and the potassium-nitrate method, while originally intended to determine true acidity, actually determines active aluminum. Since acid phosphate has some free phosphoric acid the first two methods will record increased acidity as the amount of acid phosphate is increased.

Hartwell and Pember (27) also observed that in spite of the large amount of acidity (as determined by calcium acetate) due to acid phosphate, barley made a marked growth. In the present investigation the growth of sweet clover on pots receiving acid phosphate alone increased as the acid phosphate applied increased. But the correlation is between growth and decrease of acidity rather than growth and increase of acid phosphate. This is better

¹ W. Albert Albrecht's unpublished work in the University of Illinois.

illustrated in table 8 in which the per cent of acidity reduced and the dry matter of five plants from each pot are put together.

The results given are one of the evidences that aluminum is an important factor in the acidity of the three types of soil studied.

TABLE 8

Effect of the reduction of acidity by acid phosphate on the yield of sweet clover
Gray silt

Pot number.....	701	705	706	707
Per cent of acidity reduced.....		16.16	5.70	24.19
Dry weight (gm.).....	0.54	0.87	0.58	1.12

Yellow gray silt

Pot number.....	801	805	806	807
Per cent of acidity reduced.....		21.37	11.65	42.28
Dry weight (gm.).....	0.27	0.40	0.23	0.67

Yellow slit

Pot number.....	901	905	906	907
Per cent of acidity reduced.....		4.18	1.36	17.45
Dry weight (gm.).....	0.52	0.75	0.62	1.21

Experiment III. What happens when acid soils are leached out with potassium nitrate or water

Two pots of each of the three types of soil were leached out with normal potassium nitrate until the last 125 cc. of leachings were practically neutral. With the gray silt loam 30 liters of the solution per pot were needed to reach this point. For the yellow gray silt loam 35 liters were needed, and for the yellow silt 39 liters. After leaching with potassium nitrate the soil was leached out with distilled water again in order to get rid of the excess of potassium nitrate. The leaching was continued also until the last few drops showed faintly blue to the diphenylamine sulfuric acid test for nitrates. Then the soils were dried out and sampled for analysis. The results of the analysis are given in column 3, table 4.

A similar set was leached out with water alone. Distilled water was used in leaching the soils and the operation was continued until the last 125 cc. needed hardly 0.5 cc. of the standard sodium hydroxide solution used in titrating the acidity. When this end was reached, 12 liters of water had been used in the gray silt; 16 liters in the yellow gray silt; and 13 liters in the yellow silt. Then the soil was dried and sampled as in the above set for analysis. The results of the analysis are given in column 5, table 4.

What has been found from the above experiments may be summarized as follows. With potassium nitrate 96.96 per cent of the acidity of the gray silt

was extracted, with water only 7.31 per cent of the acidity was extracted. Of the aluminum 44.79 per cent was leached out by potassium nitrate and 17.67 per cent by water; of the iron 23.85 per cent was leached out by potassium nitrate and 7.53 per cent by water; of the manganese 4.76 per cent and 1.19 per cent were leached out by potassium nitrate and water, respectively. Potassium increased 28.95 per cent and nitrate nitrogen 20.69 per cent.

With the yellow gray silt 99.15 per cent of the acidity was extracted by potassium nitrate and 7.21 per cent by water; 59.93 per cent of the aluminum was leached out by potassium nitrate and 24.73 per cent by water; 14.44 per cent of the iron was leached out by potassium nitrate and 2.48 per cent by water; and of manganese 3.03 per cent and 1.03 per cent was leached out by potassium nitrate and water, respectively. Potassium was increased 25.72 per cent and nitrate nitrogen 55.60 per cent.

With the yellow silt, potassium nitrate extracted 97.93 per cent of the acidity, and water 12.36 per cent; of aluminum 50.61 per cent was leached out by potassium nitrate and 21.55 per cent by water; of iron 21.01 per cent was leached out by potassium nitrate and 8.62 per cent by water; of manganese 8.79 per cent was extracted by potassium nitrate and 1.51 per cent by water. Potassium was increased by 28.57 per cent and nitrate nitrogen by 90.47 per cent. It may be added that potassium nitrate also leached out some of the calcium and phosphorus of the soils.

Discussion of results. These results reveal the fact that from 44 to 60 per cent of the aluminum in the soil may be leached out by potassium nitrate and that the leaching of this amount is accompanied by a big decrease in the acidity. Thus the 44.79 per cent of aluminum leached out from the gray silt was accompanied by the disappearance of 96.96 per cent of the acidity. In the case of the yellow gray silt the extraction of 59.93 per cent was accompanied by the destruction of 99.15 per cent of the acidity. With the yellow silt 50.61 per cent of the aluminum extracted was equivalent to a 97.93 per cent decrease in the acidity. It is not to be expected to extract all the aluminum in order to reduce the acidity of the soil to zero, for not all the aluminum in the soil is in the form readily soluble in potassium-nitrate solution. Some of the aluminum is present as silicate and since clay constitutes from 10.15 to 26.4 per cent of the bulk of the soils under experiment, it is not unlikely that kaolinite, $Al_2(OH)_3Si_2O_5$, the chief constituent of clay, is present in considerable amounts. Kaolinite is a very stable compound, and although kaolin (70), a mechanical mixture of kaolinite and silica, has been found to exchange bases with salt solutions, nevertheless, under the conditions in which the aluminum has been leached out in the present work, it is not probable that kaolinite and allied aluminum minerals will be readily attacked by potassium nitrate solutions. The case is more likely to be that a considerable amount of soluble aluminum compounds—salts and the trihydroxides—are present in the soil. In contact with potassium nitrate or even with water these compounds readily go into solution and are leached out. The 40 or 60 per cent of aluminum

leached out represents these soluble compounds or active aluminum. This active aluminum is equivalent approximately to 53,240 and 90,720 pounds per acre, respectively.

In the case of the water-leached soils it is seen that from 17.67 per cent to 24.73 per cent of the aluminum is leached out. These percentages are equivalent approximately to 20,570 pounds and 26,388 pounds per acre, respectively. The quantity of aluminum found in the water leachings would not probably be the actual amount of soluble aluminum in the field because certain factors, such as the transporting, storing and drying of the soil when brought to the greenhouse, might have contributed to the increase of the solubility of aluminum, but allowing 50 per cent to these factors we have still about 10,000 or 18,000 pounds left to be assigned to the readily soluble aluminum in the soils. The amount of aluminum in the maximum application of aluminum nitrate in the sand series is equivalent to 2701 pounds only, and this proved fatal to sweet clover. In the normal application of the same salt the aluminum is equivalent to 540 pounds per acre only, yet this proved toxic to sweet clover. If this is true what a tremendous influence will 10,000 or 18,000 pounds have on the crop in the field.

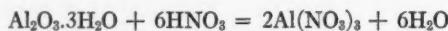
Sweet clover on the leached-out soils. Sweet clover seeds were sown in both potassium-nitrate-leached and water-leached soils. In the case of the former there were some difficulties which were never overcome in the case of two soils up to the writing up of this work. First, too much potassium nitrate was left in the soils in spite of the leaching by water. Gray silt loam had 28.69 per cent more nitrate nitrogen and 28.95 per cent more potassium than the original. Yellow gray silt loam had 55 per cent more nitrate nitrogen, and 25.72 per cent more potassium than the original; and the yellow silt had 90.27 per cent more nitrate nitrogen and 28.57 per cent more potassium. The second difficulty was the physical texture of the soils which was badly affected by the leaching with potassium nitrate. The soils became more compact and sticky. The first planting was consequently a failure. An attempt has been made to improve the physical texture of the soil by mixing the soil with one-third of its volume of pure silica sand and leaching out with water again. But the nitrate remaining was still in large enough amounts to be fatal to seedlings, consequently the second planting was again a failure. The soils were laid aside and watered every day until it was thought enough nitrate salt had been drained out. Seeds were then planted. At the beginning the seedlings seemed to be making headway, but within three weeks the seedlings in the yellow gray and yellow silt loams were already either dead or dying. Evidently the concentration of salts in these two types of soil was still too strong for the plants to survive. In the case of the gray silt the seedlings persisted and grew, although slowly. The growth up to May 19, at the age of 120 days, is shown in plate 9. A, is water-leached soil, A-1 is potassium-nitrate-leached soil, A-2 original soil plus KNO_3 equivalent to the excess found in the KNO_3 -leached soil plus sand, A-3, the original soil plus sand. Attention

is called to the difference of the growth of sweet clover on the different pots. The plants in the potassium-nitrate-leached soil, although somewhat stunted in growth, were really healthy and deep green. The plants in A-2 and A-3 were largely chlorotic. This difference in the growth is attributed to the reduction of 96 per cent of the acidity of the soil, which is equivalent to 53,240 pounds of aluminum removed. It is also important to note the growth of sweet clover on the water-leached soil. Although only 96 days old they looked just as vigorous as those in the potassium-nitrate-leached soil. This was due chiefly to the presence of a still excessive amount of the nitrate salt in the potassium-nitrate-leached soil. But it is evident that the removal of about 20,000 pounds of aluminum by water had greatly benefited the growth of sweet clover and this amount was probably the amount of active aluminum immediately concerned in the unproductivity of the soils under investigation. This effect of the removal of about 44 per cent of aluminum in the soil by potassium nitrate and 17 per cent by water, on the growth of sweet clover, is conclusive proof that aluminum is the chief factor in the unproductivity of the three types of soil under investigation and probably of most acid soils in America.

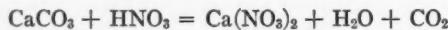
How aluminum salts arise in the soil. The form of aluminum immediately concerned in the behaviour of sweet clover toward acid soils is the soluble form, the salts. The silicates and hydroxides cannot produce toxicity inasmuch as they are insoluble in water. In the case of one form of hydroxide, the monohydroxide, it has been proven harmless to sweet clover in the present investigation. But the salts have been proven injurious to plants even in dilute solutions.

The question now arises as to how aluminum salts may be formed in the soil. Aluminum chloride, sulfate and nitrate may all be found in the soil. The amount of aluminum chloride will naturally be limited by the absolute amount of chlorine in the soil. Aluminum sulfate will also be limited by the amount of sulfur. Under certain conditions, if the soil is rich in sulfur and the sulfur bacteria are active, through sulfification considerable amounts of aluminum sulfate may be formed. Investigating the effect of sulfification on the availability of potassium in the soil, Ames and Boltz (2) found that aluminum was not present in the extract of soils in which sulfur did not enter as a part of the treatment, and concluded that aluminum sulfate is formed during sulfification. Artificial treatment of the soil may give rise to considerable amounts of aluminum sulfate. Ruprecht and Morse (60) found that the continuous application of ammonium sulfate to plots in the experimental field in Massachusetts produced aluminum sulfate. But great as is the possibility of the formation of aluminum sulfate in large quantities, still greater is the possibility for the formation of aluminum nitrate. Nitrification is a normal process occurring in the soil, and depending on conditions it varies widely. At certain seasons of the year nitrification is most active. Such is the condition under which large quantities of aluminum nitrate may be formed. In

normal soils, sufficiently provided with limestone, aluminum salt may never be formed, but in soils deficient in limestone, aluminum salts are largely formed; especially is it true when nitrification is most active. The acid-soluble aluminum trihydroxide in the soil, in the absence of limestone and other suitable bases, unites with nitric acid forming aluminum nitrate. The reaction may be represented by the following equation:

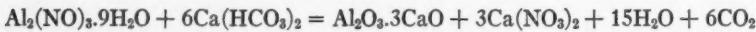


If limestone is present in sufficient quantities to satisfy the basic need of nitric acid produced, aluminum nitrate and sulfate may never be formed. Calcium nitrate, the best form of nitrogen compound for plant-food is formed, instead, according to the following reaction:

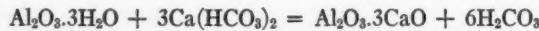


Ames and Boltz (2) noted that the largest amount of aluminum was found in solutions from soils where sulfur was oxidized in the absence of calcium carbonate.

What happens when acid soils are extracted with potassium nitrate before and after the application of limestone. The fact has been repeatedly observed in the present investigation that when an acid soil was extracted with potassium nitrate the reaction of the extract was always acid, but when limestone (calcium carbonate) was applied in amounts equivalent to or five times the lime requirement, and the soil was extracted with potassium nitrate the reaction of the extract was always alkaline and the white gelatinous aluminum hydroxide precipitate was absent. Knight² found that "when a base is added to an acid soil, comparatively insoluble products are formed. Calcium produces a product less soluble than does potassium." Ames and Boltz (2) also found that the addition of calcium carbonate at the rate of 80,000 parts per million on the soil, decreased the solubility of aluminum to 68 parts per million as compared with 660 parts per million where calcium was added in amounts just sufficient to combine with only a small part of the sulfuric acid. What most probably happens is this: When calcium carbonate is applied to the soil, calcium bicarbonate is formed which unites with the aluminum salts or with the acid-soluble hydroxide, forming calcium aluminate, a stable compound. The reaction may be written as follows:



or



When an acid soil comes in contact with potassium nitrate solution an exchange of bases between the soil and the solution takes place (70). The

² H. G. Knight, "Acidity and Acidimetry of Soil," unpublished thesis from the University of Illinois.

aluminum compounds are attacked, bringing aluminum into solution and forming aluminum nitrate which on hydrolysis produces strong acidity. This is the cause of the acid reaction of the solution. When an acid soil is treated with calcium carbonate and after a while extracted with potassium nitrate the extract is alkaline. An exchange of bases takes place also. But in this case the calcium compounds formed in the soil are attacked by the salt solution, calcium being replaced by potassium and brought into solution as calcium nitrate. Such an explanation is in agreement with the findings of van Bemmelen (5) and other investigators (70) on the subject of exchange of bases between soils and salt solutions, the former having found that when potassium chloride solution was added to the soil, almost a complete change of potassium for calcium and magnesium took place. The presence of calcium nitrate, therefore, which does not hydrolyze, explains the neutral or alkaline reaction of the extract.

Experiment IV. Iron and manganese as factors in soil acidity

The table of analysis reveals that the types of soil under investigation also contain considerable quantities of iron and manganese. The gray silt contains 47,800 pounds of iron and 840 pounds of manganese per acre. The yellow gray silt contains 40,300 pounds of iron and 786 pounds of manganese per acre; and the yellow silt contains 74,200 pounds of iron and 660 pounds of manganese per acre. The toxicity of normal iron salts at a certain concentration is well known, and Ruprecht and Morse (61) found that in the unproductivity of ammonium-sulfate fertilized plots of the Massachusetts Agricultural Experiment Station, ferric and manganese salts were also contributing factors. Funchess (20) also observed that in Alabama the development of soluble manganese salts was the cause of the unproductivity of a certain soil. The question now comes up as to whether iron and manganese might not be also contributing factors in the acidity of the soils under investigation. It was thought that if these metals were as important a factor as aluminum, some idea might be obtained from their degree of solubility and their ratio to soluble aluminum. Fortunately, the first 4-liter potassium-nitrate leachings of the gray silt and the first 4-liter water-leachings of the three types of soil have been saved. These leachings were analyzed for aluminum, iron and manganese. The results of the analysis are given in table 9.

This table shows that the ratio of aluminum, iron and manganese in the first 4 liters of the potassium-nitrate leachings is 4.6:1:1.2. The first 4 liters of water extract gave for the gray silt loam 4.8 for aluminum, 1 for iron and 1.1 for manganese; for the yellow gray silt loam 6.2 for aluminum, 1 for iron and 1.3 for manganese; and for the yellow silt 3.4 for aluminum, 1 for iron and 1.7 for manganese. The proportion of aluminum to iron or manganese is such that there can be no doubt that aluminum is the dominant factor. In the case of manganese a further step has been taken. Sand-culture experiments were

carried out with manganese sulfate, nitrate and carbonate, the plan being the same as that in the aluminum series. The results of these experiments reveal that manganese cannot be any factor in the soil in question for this reason. When calcium carbonate in considerable quantities was combined with aluminum salts the toxicity of the aluminum was corrected. In the case of the soils, calcium carbonate also corrected their acidity or unproductivity, but with manganese compounds not even the application of five times the lime requirement of calcium carbonate has corrected the toxicity of manganese. It is not denied that iron and manganese might become factors in the acidity of some soils but with the soils under investigation there is no doubt that aluminum is the determining factor in their acidity.

TABLE 9
Analysis of extracts (4 liters)

TYPE OF SOIL	DETERMINED		
	Aluminum	Iron	Manganese
<i>KNO₃ extract</i>			
Gray silt (mgm.).....	282.5	60.9	49.8
Ratio.....	4.6	1	1.2
<i>H₂O extract</i>			
Gray silt (mgm.).....	75.5	15.8	14.6
Ratio.....	4.8	1	1.1
Yellow gray silt (mgm.).....	105.2	17.0	13.1
Ratio.....	6.2	1	1.3
Yellow silt (mgm.).....	88.9	26.3	16.3
Ratio.....	3.4	1	1.7

V. SUMMARY

Experiments have been carried out, first, to find out the influence of aluminum salts and aluminum hydroxide, alone and in combination with calcium carbonate or with acid phosphate, on the growth of sweet clover grown in sand; second, to determine the effect of limestone and acid phosphate alone and in combination, on the productivity and acidity of three types of silt loam soil; third, to find out the effect of the removal of some aluminum from the soil on the growth of sweet clover; and fourth, to ascertain whether iron and manganese also are factors in the acidity of the soils under investigation.

In the absence of some calcium compounds as a source of calcium, aluminum salts were highly toxic to sweet clover when applied in amounts chemically equivalent to the acidity of the soil, and fatal to sweet clover when applied in

amounts chemically equivalent to five times the acidity of the soil. In the presence of calcium silicate, aluminum nitrate was more toxic than aluminum sulfate.

Aluminum mono-hydroxide had no effect whatever on the growth of sweet clover, when other plant-food elements were added in water-soluble form.

Calcium carbonate in sufficient amounts corrected the toxicity of aluminum salts, by precipitating aluminum as calcium aluminate, an insoluble compound.

Acid phosphate applied at the rate of 400 pounds per acre reduced the toxicity of aluminum salts by forming aluminum phosphate, an insoluble aluminum compound.

Limestone applied at a rate equal to the lime requirement produced good crops on the three silt loam soils; applied at the rate of five times the lime requirement it produced better crops. At the same rate of application the soils were alkaline at the end of 178 days. The action of calcium carbonate in the soil is to unite with the aluminum salts and the acid-soluble aluminum hydroxide, forming calcium aluminate.

Acid phosphate applied alone at the rate of 1 ton to the acre produced fair crops, at the rate of 5 tons good crops. Acid phosphate also reduced the acidity of the soils and the decreases depended on the rate of application. At the rate of 5 tons per acre acid phosphate reduced the acidity of the soils from 51 to 57 per cent. The reduction of the acidity was due to the formation of the insoluble aluminum phosphate.

The combination of acid phosphate and limestone in large quantities produced the best crops.

The aluminum in the soil varies from 121,000 to 151,000 pounds per acre. When the soil was leached out with potassium nitrate solution until the last 125 cc. of leachings was practically neutral, the acidity of the soil was reduced 99 per cent and as much as 59 per cent of the aluminum was leached out. Sweet clover growing on leached soil was better than that growing on unleached soil. The fact conclusively proved that aluminum is the determining factor in the acidity of the soils under investigation and probably of most other acid soils of the same origin.

The form of aluminum immediately concerned in the unproductivity of acid soils in the soluble form, is the salts. These salts are derived from the acid-soluble aluminum hydroxide, or gibbsite. In soils sufficiently provided with calcium, toxic aluminum salts may never be formed, but in soils deficient in calcium and other bases, as in the case of acid soils, toxic aluminum salts are largely the end-products of sulfification and nitrification.

It is not denied that iron and manganese may become contributing factors in the unproductivity of some acid soils, but the preponderance of evidence points to aluminum as the determining factor in the acidity of the soils under investigation.

The potassium nitrate extract of an acid soil is acid, but the same extract after sufficient amounts of limestone have been applied to the soil is alkaline.

In the first case an exchange of bases takes place between the aluminum compounds and the potassium-nitrate solution bringing aluminum into solution and forming aluminum nitrate, which on hydrolysis produces strong acidity. This is the cause of the acid reaction of the solution. In the second case an exchange of bases also takes place, but this time between the calcium compounds and the potassium nitrate solution, bringing calcium into solution and forming calcium nitrate. This compound is not hydrolyzed and therefore will not produce acidity. This explains the neutral or alkaline reaction of the extract.

In so far as aluminum is a factor in soil acidity the Hopkins method is the best one for soil-acidity determinations. It determines active aluminum and under field conditions when the lime requirement of the soil has been satisfied with the amount of calcium carbonate as determined by the method, the toxicity of aluminum is eliminated.

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PLATE 1

EFFECT OF ALUMINUM SULFATE ON THE GROWTH OF SWEET CLOVER

FIG. 1. First crop, 93 days old.

- 101—Control—plant-food only.
- 102—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre.
- 103—Plant-food plus 620 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre.
- 104—Plant-food plus 15,500 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre.
- 105—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 2716 pounds of CaCO_3 .
- 106—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 543 pounds of CaCO_3 .
- 107—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ plus 13,580 pounds of CaCO_3 .
- 108—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 1054 pounds of CaCO_3 .
- 109—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 211 pounds of CaCO_3 .
- 110—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 5270 pounds of CaCO_3 .

FIG. 2. Second crop, 96 days old. The same as above plus CaSiO_3 and acid phosphate, reduced from 100 to 400 pounds per acre.

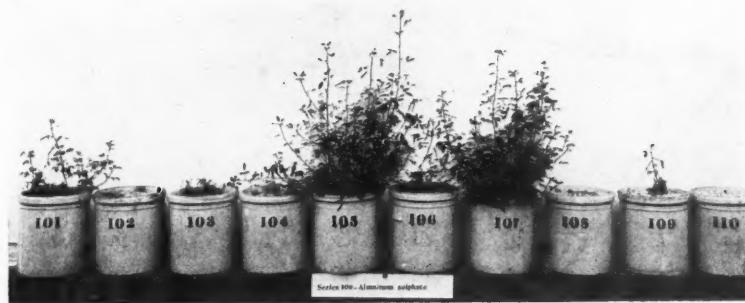


FIG. 1

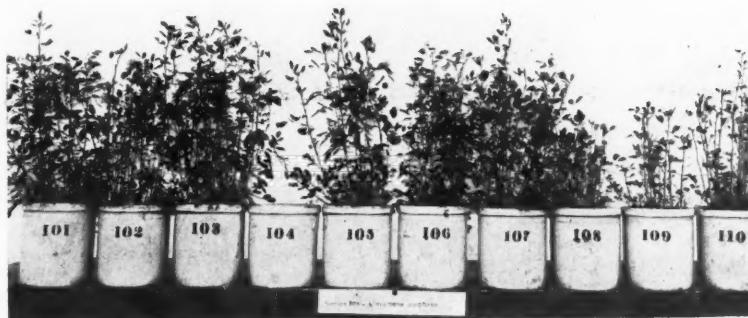


FIG. 2

PLATE 2

EFFECT OF ALUMINUM CHLORIDE ON SWEET CLOVER

FIG. 1. Sweet clover at the age of 44 days.

201—Control—Plant-food only.
202—Plant-food plus 2405 pounds of AlCl_3 per acre.
203—Plant-food plus 461 pounds of AlCl_3 per acre.
204—Plant-food plus 12,025 pounds of AlCl_3 per acre.
205—Plant-food plus 2405 pounds of AlCl_3 plus 2716 pounds of CaCO_3 per acre.
206—Plant-food plus 2405 pounds of AlCl_3 plus 543 pounds of CaCO_3 per acre.
207—Plant-food plus 2405 pounds of AlCl_3 plus 13,580 pounds of CaCO_3 per acre.
208—Plant-food plus 2405 pounds of AlCl_3 plus 1054 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.
209—Plant-food plus 2405 pounds of AlCl_3 plus 211 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.
210—Plant-food plus 2405 pounds of AlCl_3 plus 5270 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

FIG. 2. Same, at the age of 93 days. Treatment, same as above.

ALUMINUM AS A FACTOR IN SOIL ACIDITY
JOSE JISON MIRASOL

PLATE 2



FIG. 1



FIG. 2

PLATE 3

EFFECT OF ALUMINUM NITRATE ON SWEET CLOVER

FIG. 1. First crop, 93 days old.

301—Control—Plant-food only.

302—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per acre.

303—Plant-food plus 752 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per acre.

304—Plant-food plus 19,295 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per acre.

305—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 2716 pounds CaCO_3 per acre.

306—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 543 pounds of CaCO_3 per acre.

307—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 13,580 pounds of CaCO_3 per acre.

308—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 1054 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

309—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 211 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

310—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 5270 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

FIG. 2. Second crop, 96 days old. Same as above with the same changes as noted in series 100.



FIG. 1

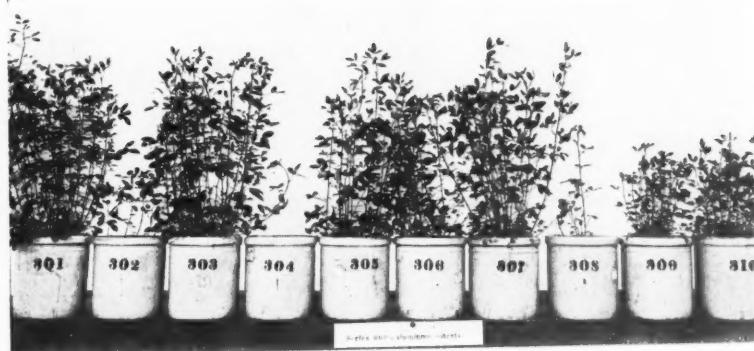


FIG. 2

PLATE 4

EFFECT OF ALUMINUM HYDROXIDE ON SWEET CLOVER

FIG. 1. First crop, 93 days old.

- 401—Control—Plant-food only.
- 402—Plant-food plus 1399 pounds of Al(OH)_3 per acre.
- 403—Plant-food plus 280 pounds of Al(OH)_3 per acre.
- 404—Plant-food plus 6995 pounds of Al(OH)_3 per acre.
- 405—Plant-food plus 1399 pounds of Al(OH)_3 plus 2716 pounds of CaCO_3 per acre.
- 406—Plant-food plus 1399 pounds of Al(OH)_3 plus 543 pounds of CaCO_3 per acre.
- 407—Plant-food plus 1399 pounds of Al(OH)_3 plus 13,580 pounds of CaCO_3 per acre.
- 408—Plant-food plus 1399 pounds of Al(OH)_3 plus 1054 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.
- 409—Plant-food plus 1399 pounds of Al(OH)_3 plus 211 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.
- 410—Plant-food plus 1399 pounds of Al(OH)_3 plus 5270 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

FIG. 2-3. Second crop, 96 days old. Same as above up to 410 with the same changes as noted in series 100 to 300.

- 411—Plant-food plus 1399 pounds of Al(OH)_3 plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.
- 412—Plant-food plus 1399 pounds of Al(OH)_3 plus 160 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.
- 413—Plant-food plus 1399 pounds of Al(OH)_3 plus 4000 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.
- 414—Plant-food plus 6995 pounds of Al(OH)_3 plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.
- 415—Plant-food plus 1399 pounds of Al(OH)_3 plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ plus 2716 pounds of CaCO_3 per acre.
- 416—Plant-food plus 1399 pounds of Al(OH)_3 plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ plus 543 pounds of CaCO_3 per acre.
- 417—Plant-food plus 1399 pounds of Al(OH)_3 plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ plus 13,580 pounds of CaCO_3 per acre.
- 418—Plant-food plus 1399 pounds of Al(OH)_3 plus 2423 pounds of dried blood per acre.
- 419—Plant-food plus 1399 pounds of Al(OH)_3 plus 484 pounds of dried blood per acre.

ALUMINUM AS A FACTOR IN SOIL ACIDITY
JOSE JISON MIRASON

PLATE 4



FIG. 1



FIG. 2

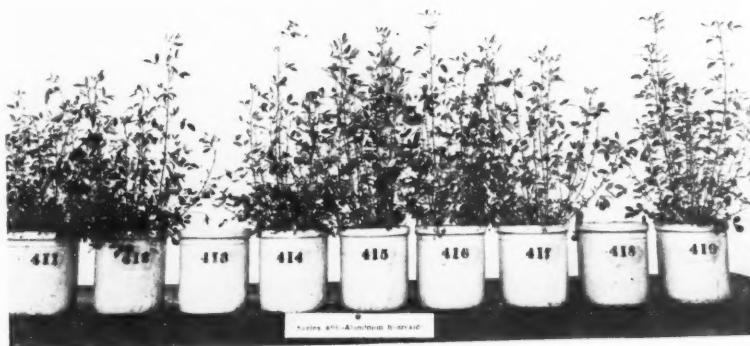


FIG. 3

PLATE 5

EFFECT OF ACID PHOSPHATE ON SWEET CLOVER

FIG. 1. First crop, 75 days old.

601—Control—Plant-food only.

602—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ per acre.

603—Plant-food plus 193 pounds of $\text{CaH}_4(\text{PO}_4)_3$ per acre.

604—Plant-food plus 4820 pounds of $\text{CaH}_4(\text{PO}_4)_3$ per acre.

605—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ plus 2921 pounds of CaCO_3 per acre.

606—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ plus 584 pounds of CaCO_3 per acre.

607—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ plus 14635 pounds of CaCO_3 per acre.

FIG. 2. Second crop, 67 days old. Amounts of acid phosphate reduced to from 100 to 400 pounds per acre.

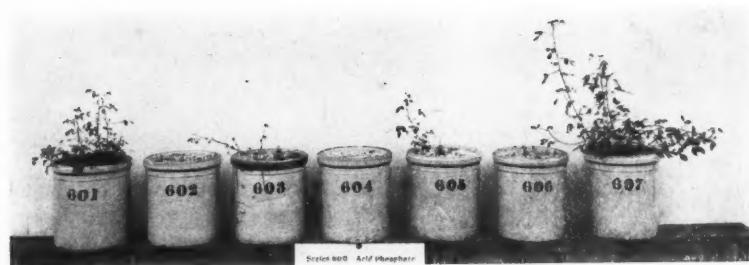


FIG. 1



FIG. 2

PLATE 6

EFFECT OF LIMESTONE AND ACID PHOSPHATE ON THE PRODUCTIVITY OF GRAY SILT LOAM

FIG. 1. First crop, 98 days old.

701—Control.

702—2125 pounds of limestone per acre.

703—425 pounds of limestone per acre.

704—10,625 pounds of limestone per acre.

705—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

706—462 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

707—11,550 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

708—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2125 pounds of limestone per acre.

709—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 425 pounds of limestone per acre.

710—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 10,625 pounds of limestone per acre.

FIG. 2. Second crop, 123 days old. Treatment, same as above.

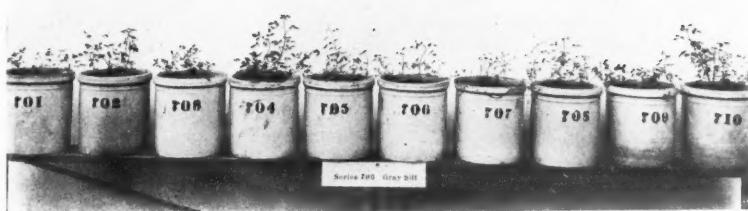


FIG. 1



FIG. 2

PLATE 7

EFFECT OF LIMESTONE AND ACID PHOSPHATE ON THE PRODUCTIVITY OF YELLOW GRAY SILT LOAM

FIG. 1. First crop, 98 days old.

801—Control.

802—2813 pounds of limestone per acre.

803—562 pounds of limestone per acre.

804—14,065 pounds of limestone per acre.

805—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

806—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

807—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

808—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2813 pounds of limestone per acre.

809—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 562 pounds of limestone per acre.

810—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,065 pounds of limestone per acre.

FIG. 2. Second crop, 123 days old. Treatment, same as above.



FIG. 1



FIG. 2

PLATE 8

EFFECT OF LIMESTONE AND ACID PHOSPHATE ON THE PRODUCTIVITY OF YELLOW SILT LOAM

FIG. 1. First crop, 98 days old.

901—Control.

902—2921 pounds of limestone per acre.

903—584 pounds of limestone per acre.

904—14,605 pounds of limestone per acre.

905—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

906—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

907—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

908—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2921 pounds of limestone per acre.

909—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 584 pounds of limestone per acre.

910—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,605 pounds of limestone per acre.

FIG. 2. Second crop, 123 days old. Treatment, same as above.



FIG. 1



FIG. 2

PLATE 9

SWEET CLOVER ON POTASSIUM-NITRATE AND WATER-LEACHED GRAY SILT LOAM SOIL

- A. Water-leached soil.
- A-1. Potassium-nitrate-leached soil.
- A-2. Original soil plus KNO_3 equal to excess of KNO_3 in A-1.
- A-3. Original soil.



PLATE 10

GRAPHS SHOWING THE DECREASE OF ACIDITY OF SOIL DUE TO TREATMENT—GRAY
SILT LOAM

Curve 1 represents the per cent decrease of acidity in 108 days; curve 2 the per cent decrease in 178 days.

701—Control

702—2125 pounds of limestone per acre.

703—425 pounds of limestone per acre.

704—10,625 pounds of limestone per acre.

705—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

706—462 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

707—11,550 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

708—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2125 pounds of limestone per acre.

709—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 425 pounds of limestone per acre.

710—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 10,625 pounds of limestone per acre.

ALUMINUM AS A FACTOR IN SOIL ACIDITY
JOSE JISON MIRASOL

PLATE 10

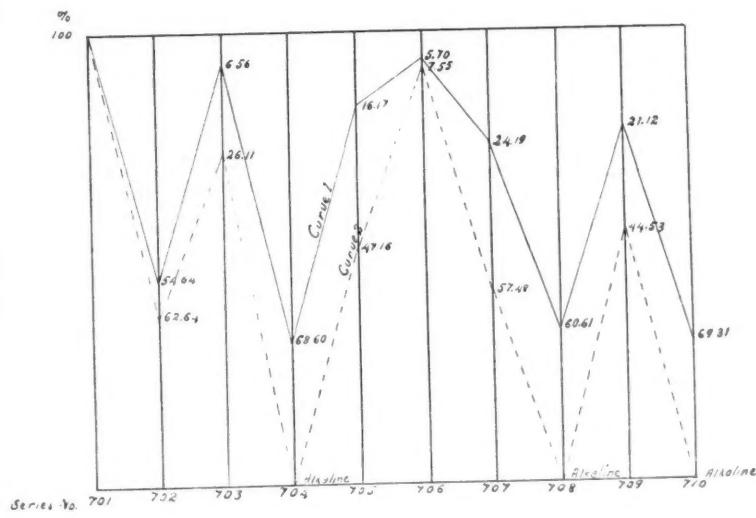


PLATE 11

GRAPHS SHOWING THE DECREASE OF ACIDITY OF SOIL DUE TO TREATMENT—YELLOW
GRAY SILT LOAM

Curve 1 represents the per cent decrease of acidity in 108 days; curve 2 the per cent decrease of acidity in 178 days.

801—Control.

802—2813 pounds of limestone per acre.

803—562 pounds of limestone per acre.

804—14,065 pounds of limestone per acre.

805—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

806—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

807—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

808—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2813 pounds of limestone per acre.

809—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 562 pounds of limestone per acre.

810—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,065 pounds of limestone per acre.

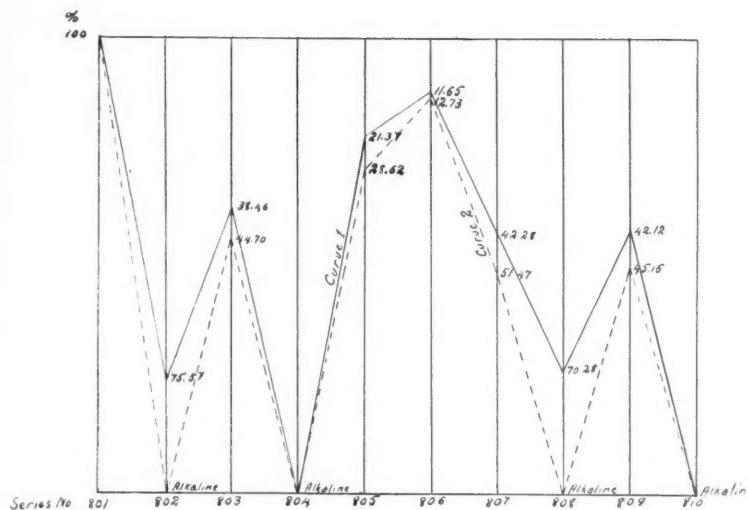


PLATE 12

GRAPHS SHOWING THE DECREASE OF ACIDITY OF SOIL DUE TO TREATMENT—YELLOW
SILT LOAM

Curve 1 represents the per cent decrease of acidity in 108 days; curve 2 the per cent decrease of acidity in 178 days.

901—Control.

902—2921 pounds of limestone per acre.

903—584 pounds of limestone per acre.

904—14,605 pounds of limestone per acre.

905—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

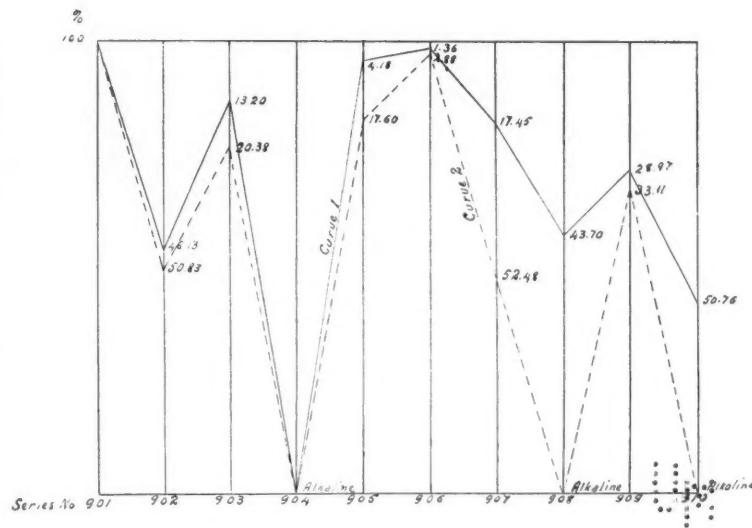
906—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

907—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

908—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2921 pounds of limestone per acre.

909—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 594 pounds of limestone per acre.

910—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,605 pounds of limestone per acre.



THE FORMATION OF SOLUBLE SUBSTANCES IN SOILS TAKEN FROM WIDELY SEPARATED REGIONS

M. M. McCool AND C. E. MILLAR

Michigan Agricultural Experiment Station

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The rate of formation of soluble substances in soils has received a great deal of study by various members of the Soils Section. The freezing-point method, perfected by Bouyoucos (1), in the main has been utilized for these investigations, yet the composition of the material going into solution has received attention (7). Our plans call for extensive researches along these lines. Millar is investigating the composition of the soil solution of cropped and virgin soils, while Spurway (9) and Wheating, respectively, are considering the residuary effects of salts on soils of different texture.

In discussing with Prof. C. F. Marbut, of the United States Bureau of Soils, the origin, weathering, composition and other questions that arise in connection with the soil survey work, it occurred to us that an investigation of the relative rate of formation of soluble salts in soils derived from material of different nature and formed under various climatic conditions as well as in soils which might be classed as very old, intermediate, and young, would be interesting and profitable. Accordingly through the courtesy of Professor Marbut and several members of the corps of field men engaged in soil survey work, a number of such samples were obtained. Many samples were supplied also by the men in charge of the soils work and outlying experimental stations of several states. Samples were received from the following states: Texas, Ohio, California, Washington, Arizona, Kentucky, Nevada, Tennessee, Michigan, Kansas, Indiana, Missouri, Georgia and Alabama. A brief description of the soil and subsoil follows the name used to characterize each sample. The numbers correspond to those on the map and those preceding the soil names in the tables of data. Unless otherwise indicated the surface samples were taken to a depth of 8 inches and the subsoils from 24 to 36 inches. The regions from which the samples were obtained are shown on the accompanying sketch map.

DESCRIPTION OF SOILS

1. *Cochise, Arizona.* This is a chocolate-brown clayey sand containing much coarse material. The subsoil is a calcareous red clay intermixed with much coarse material. This sample is from the Sulfur Springs Valley dry farm which has an elevation of about 4,000 feet and an annual precipitation of approximately 11 inches.

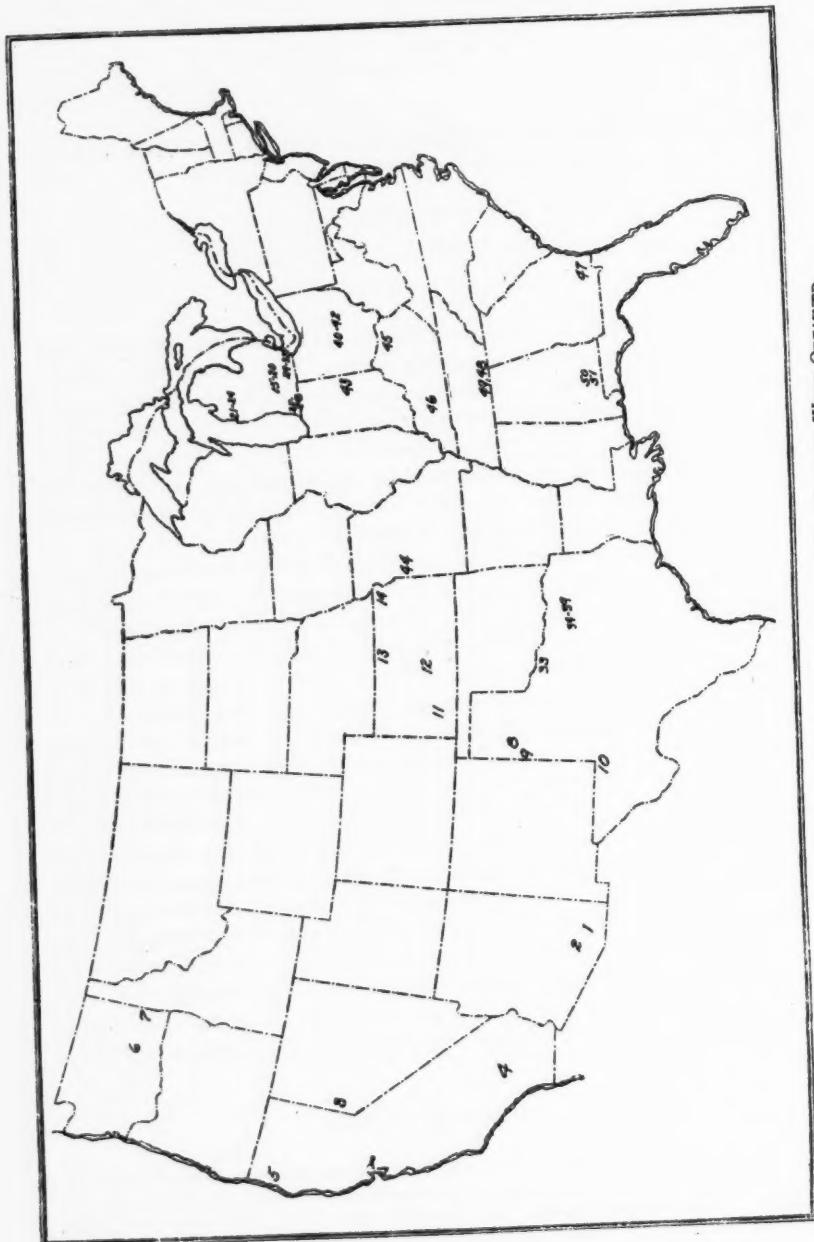


FIG. 1. MAP SHOWING REGIONS FROM WHICH SOIL SAMPLES WERE OBTAINED

2. *Tucson, Arizona.* The soil consists of calcareous gray fine sand. The subsoil is of similar material. This soil represents a virgin area in the Rilleto River bottom on the University Farm. The rainfall in this locality is between 11 and 12 inches and the elevation is about 2300 feet.

3. *Reno, Nevada.* This is a brown sandy loam with a brown sandy loam subsoil. This sample was taken from the Experiment Station farm which is under irrigation.

4. *Whittier, California.* This is a clay loam with a dark gray clay subsoil and was derived from shale, sandstone and other metamorphic rocks. Depth of sample: surface 12 inches; subsoil 24 inches.

5. *Riverside, California.* Classified as Placentia light sandy loam with a coarse brown sandy loam subsoil. This soil is of granitic origin. Depth of sample: surface 12 inches; subsoil 12 to 24 inches.

6. *Lind, Washington.* This is a very fine sand with a yellow very fine sandy loam subsoil.

7. *Pullman, Washington.* This soil is a dark silt loam with a yellow clay subsoil.

Texas soils

8. *Spur.* This is a chocolate-brown clay with a reddish brown clay subsoil. The sample was taken from a virgin area on the experiment station farm.

9. *Lubbock.* 1. This soil is classified by the Bureau of Soils as Armarillo fine sandy loam. The subsoil is a calcareous brown fine sandy loam underlaid with marl at from 3 to 4 feet.

9a. *Lubbock.* 2. A heavy fine sandy loam classified by the Bureau of Soils as Richfield loam. The subsoil is a calcareous heavy sandy loam underlaid with marl at from 2 to 4 feet.

10. *Pecos.* This is a gray light sandy loam with a gray sandy clay subsoil. The sample represents a virgin area on the Experiment Station farm.

Kansas soils

11. *Richland silt loam.* The sample was taken from an irrigated field in Finney County. It has grown grain crops for 20 years. Depth of sample: surface 7 inches.

12. *Arkansas fine sandy loam.* This soil represents the bottom land along the Arkansas River. The sample was taken from a field in Pawnee County which has been cropped for 20 years. The water-table comes to within about 4 feet of the surface. Depth of sample: surface 7 inches.

13. *Lincoln silt loam.* This soil came from Jewell County and is considered the best general farming soil in the county. The sample came from a field which has grown corn and wheat for 30 years. Depth of sample: surface 7 inches.

14. *Marshall silt loam.* This sample came from a field in Brown County, which has been cropped to corn, wheat and oats for 45 years. Depth of sample: surface 7 inches.

Michigan soils

15. *Miami silt loam.* A brown silt loam with a brown clay loam subsoil. This soil has been cropped many years with little effort to maintain its productivity.

16. *Miami silt loam.* Similar to the above but from an uncropped area.

17. *Miami very fine sandy loam.* A brownish gray soil with a clayey sand subsoil. Representative of a very productive type of central Michigan soil.

18. *Clyde sandy loam.* A dark gray soil with gray sandy clay subsoil.

19. *Clyde silt loam.* A very heavy gray silt loam with clay loam subsoil. Representative of small areas in central Michigan.

20. *Miami sandy loam.* A rather heavy brown sandy loam with clayey sand subsoil. Representative of much of the general farming land in central Michigan.

21. *Coloma sand*. Level to undulating land originally covered with pine timber. Subsoil quite sandy.

22. *Plainfield sand*. Terrace along the Manistee River. Subsoil medium sand.

23. *Miami silt loam*. Rolling brown silt loam underlaid with yellow, mottled clay loam.

24. *Coloma sand*. Brown sand underlaid with yellow sand. Original timber pine.

25. *Silt loam*. Rolling land formerly bearing beech and maple timber. Taken from a field quite low in organic matter. Subsoil yellow sand.

26. *Plainfield sand*. Terrace formation along Dowagiac creek. Subsoil gray sand.

27. *Coloma sand*. Rolling land originally timbered with oak. Subsoil sandy. Taken from a depleted field.

28. *Miami silt loam*. Rolling beech and maple land. Subsoil brown clay loam.

29. *Miami silt loam*. Taken from a comparatively level area which is somewhat in need of drainage. This soil has been cropped quite heavily but is still productive. Subsoil is a clay loam.

30. *Clyde silt loam*. Representative of the black silt loams of the old lake bed area of southeastern Michigan. Badly in need of drainage. Subsoil is clay loam.

31. *Miami silt loam*. Area quite rolling. Representative of morainic formations in northwestern Lenawee County. Subsoil clay.

32. *Coloma sand*. Rolling sand, subject to blowing if not properly managed. Taken from a much depleted field. Subsoil, yellow sand.

Texas soils

33. *Chillicothe*. This is a deep sandy loam with a coarse clayey sand subsoil. The sample was taken from a virgin area on the Experiment Station farm and represents the average soil on the farm.

34. *Ellis clay*. Yellowish brown clay underlaid with yellow clay containing some bluish-gray mottling. This sample was taken from uncultivated prairie growing mesquite grass. Depth of sampling unknown.

35. *Bell clay*. Black clay to the depth of 12 inches. Taken from terrace land about 10 feet above high water. A very productive soil. Subsoil is a dark bluish gray clay. Gravel is found at a depth of several feet. Depth of sampling unknown.

36. *Trinity clay*. Dark brown clay to the depth of 12 inches, representing an alluvial formation along the Trinity River. It is very productive. Subsoil is brown clay for many feet. Depth of sampling unknown.

37. *Houston clay*. A black clay 12 inches deep representing the main type of central Texas prairie. Subsoil to 36 inches is black clay containing fine particles of limestone (chalk). The original chalk material is found at a depth of 5 to 10 feet. Depth of sampling unknown.

38. *Cahaba fine sandy loam*. Brown loamy fine sand to a depth of 14 inches of terrace formation. Lower portion of surface soil is reddish in color. The subsoil to a depth of 36 inches is a dull brownish red friable clay. Depth of sampling unknown.

Ohio soils

40. *Clyde silty clay loam*. Subsoil is a mottled, drab clay.

41. *Ellsworth silt loam*. Subsoil is yellow clay. This soil was derived from the weathering of sandstone and shale.

42. *Miami silty clay loam*. Subsoil consists of yellow clay. This sample is representative of the light-colored upland soil occurring over a large part of western Ohio.

43. *Miami silt loam from Delaware County, Indiana*. Depth of sampling unknown.

44. *Summit silt loam from Cass County, Missouri*. Depth of sampling unknown.

45. *Lexington, Kentucky*. This soil is a brown silt loam with a yellow clay subsoil. It was taken from a virgin woodland pasture.

46. *Greenville, Kentucky.* The surface and subsoil of this sample both consist of yellow clay. Depth of sample: surface 8 inches; subsoil 12 to 24 inches.

47. *Norfolk fine sandy loam.* From Pierce County, Georgia. Surface sample taken to a depth of 4 inches. From 4 to 24 inches there is a stratum of yellowish gray fine sand. Below this depth the sand is mixed with more plastic material.

48. *Lebanon (Clarksville) silt loam from Tennessee.* This sample was taken near Tullahoma, Tennessee, from a forest of blackjack oak, post oak, red oak and black hickory. Depth of sample 8 inches—subsoil taken from 8 to 25 inches.

49. *Hagerstown silt loam from Tennessee.* This sample was taken near Shelbyville, Tenn., and grew the following varieties of timber, red oak, post oak, white oak, hard maple, walnut and cedar. Depth of sample 8 inches.

50. *Ruston fine sandy loam.* Sample taken near Luverne in Crenshaw County, Alabama. Depth of sample 10 inches, subsoil 10 to 36 inches. From 10 to 24 inches the material is a dull red to yellowish red fine sandy clay. From 24 to 36 inches the material is the same but the color mottled.

51. *Orangeburg fine sandy loam.* The sample was collected near Luverne, Alabama, and consists of a gray fine sandy loam merging into a light reddish color in the lower depth. Depth of sample 10 inches; subsoil 10 to 36 inches. Consists of rather compact red fine sandy clay.

EXPERIMENTAL

The investigations may be divided into three phases: first, the formation of soluble material in surface and sub-soils from regions of radically different climatic conditions; second, the formation of soluble material in the various soil separates composing the soils from different regions, also the effect of grinding the coarser separates on the formation of soluble products; third, the effect of treatment with a solution of sodium nitrate on the formation of water-soluble material in the various separates obtained from certain soils.

Formation of soluble material in surface and subsoils

The samples of air-dry soil were passed through a 1-mm. screen. About 50 gm. was then placed on filter paper in a funnel and washed with distilled water until the freezing-point depression of the soil solution in the soil was practically zero. The soil was then thoroughly mixed by placing in a tumbler and stirring, and portions placed in freezing-point tubes which were stoppered and placed in a chamber maintained at 25°C. Except in the case of very heavy soils this procedure afforded sufficient moisture so that a short column of water rose above the sample in the tube, and when this was not the case sufficient water was added to bring about the above condition. At intervals the tubes were unstoppared and the contents shaken to remove any accumulated gases and provide thorough aeration. The freezing-point lowerings were determined in the usual manner after 5, 10, 30 and 60 days, unless otherwise indicated in the tables.

Table 1 shows the results for surface soils formed from various materials and under different climatic conditions. The average annual precipitation of the regions from which the samples were collected also is shown.

TABLE 1

Rate of formation of soluble material in surface soils derived from different material and from areas of various precipitation when maintained at 25°C.*

SOILS	ANNUAL PRECIPITA- TION	FREEZING-POINT DEPRESSION				
		0 days	5 days	10 days	30 days	60 days
	inches	°C.	°C.	°C.	°C.	°C.
<i>Arizona soils</i>						
1. Cochise.....	11.00	0.000	0.003	0.010	0.010	0.008
2. Tucson.....	12.00	0.000	0.009	0.010	0.017	0.016
<i>Nevada soils</i>						
3. Reno.....	8.30†	0.000	0.002	0.012	0.014	0.027
<i>California soils</i>						
4. Whittier‡.....	13.00	0.000	0.010	0.025	0.027	0.035
5. Riverside‡.....	10.00	0.000	0.002	0.004	0.005	
<i>Washington soils</i>						
6. Lind.....	9.50	0.000	0.007	0.004	0.008	0.015
7. Pullman.....	21.64	0.000	0.014	0.010	0.019	0.034
<i>Texas soils</i>						
8. Spur.....	21.00	0.000	0.028		0.027	0.026
9. Lubbock 1.....	21.00	0.000	0.010	0.020	0.029	0.024
9a. Lubbock 2.....	21.00†	0.000	0.015	0.026	0.029	0.028
10. Pecos‡.....	21.00	0.002	0.015	0.022	0.025	0.030
		0 days	5 days	10 days	20 days	40 days
<i>Kansas soils</i>						
11. Richland silt loam.....	20.00†	0.003	0.030	0.039	0.031	0.010
12. Arkansas fine sandy loam.....	22.90	0.001	0.022	0.034	0.043	0.010
13. Lincoln silt loam.....	26.30	0.000	0.020	0.031	0.032	0.012
14. Marshall silt loam.....	33.35	0.002	0.010	0.012	0.020	0.001
<i>Michigan soils</i>						
Ingham County						
15. Miami silt loam.....	30.99	0.000	0.009	0.012	0.012	0.018
16. Miami silt loam.....	30.99	0.000	0.021	0.034	0.045	0.035
17. Miami very fine sandy loam.....	30.99	0.000	0.008	0.010	0.019	0.024
18. Clyde sandy loam.....	30.99	0.001	0.013	0.034	0.030	0.030
19. Clyde silt loam.....	30.99	0.000	0.016	0.032	0.026	0.029
20. Miami sandy loam.....	30.99	0.006	0.015	0.019	0.030	0.035
Manistee County						
21. Coloma sand.....	30.27	0.000	0.002	0.011	0.024	0.020
22. Plainfield sand.....	30.27	0.000	0.003	0.004	0.016	0.019
23. Miami silt loam.....	30.27	0.000	0.028	0.038	0.035	0.039
24. Coloma sand.....	30.27	0.000	0.011	0.013	0.011	0.010
Berrien County						
25. Silt loam.....	34.15	0.001	0.012	0.013	0.013	0.026
26. Plainfield medium sand.....	34.15	0.000	0.009	0.011	0.012	0.022
27. Coloma sand.....	34.15	0.000	0.001	0.002	0.002	0.003
28. Miami silt loam.....	34.15	0.000	0.013	0.026	0.029	0.038

TABLE 1—Continued

SOILS	ANNUAL PRECIPITA- TION <i>inches</i>	FREEZING-POINT DEPRESSION				
		0 days	5 days	10 days	20 days	40 days
		°C.	°C.	°C.	°C.	°C.
Lenawee County						
29. Miami silt loam.....	37.03	0.000	0.003	0.022	0.036	0.034
30. Clyde silt loam.....	37.03	0.000	0.014	0.021	0.031	0.016
31. Miami silt loam.....	37.03	0.000	0.017	0.037	0.038	0.038
32. Coloma sand.....	37.03	0.000	0.005	0.008	0.017	0.012
		0 days	5 days	10 days	30 days	60 days
<i>Texas soils</i>						
33. Chillicothe.....	26.29	0.000	0.008	0.023	0.033	0.017
34. Ellis clay,† Dallas County	36.00	0.000	0.023	0.029	0.046	0.049
35. Bell clay,† Dallas County	36.00	0.000	0.010	0.020	0.030	0.032
36. Trinity clay,† Dallas County	36.00	0.005	0.011	0.014	0.023	0.022
37. Houston clay,† Dallas County	36.00	0.000	0.011	0.014	0.022	0.020
38. Cohoba fine sandy loam,‡ Dallas County.....	36.00	0.000	0.003	0.005	0.006	0.008
<i>Ohio soils</i>						
40. Clyde silty clay loam.....	38.80	0.003	0.033	0.028	0.013	0.020
41. Ellsworth silt loam.....	38.80	0.001	0.006	0.007	0.027	0.027
42. Miami silty clay loam	38.80	0.000	0.021	0.037	0.052	0.040
<i>Indiana soils</i> §						
43. Miami silt loam.....	38.00	0.006	0.018	0.020	0.023	0.028
<i>Missouri soils</i> §						
44. Summit silt loam.....	38.00	0.006	0.015	0.020	0.030	0.034
<i>Kentucky soils</i>						
45. Lexington.....	44.80	0.000	0.015	0.016	0.016	0.020
46. Greenville.....	45.80	0.006	0.009	0.015	0.033	
<i>Georgia soils</i>						
47. Norfolk fine sandy loam‡	50.00	0.009	0.012	0.012	0.016	0.015

* Samples taken to depth of 8 inches unless otherwise stated.

† Soil under irrigation.

‡ See description for depth of sampling.

§ Maintained at room temperature.

There are some very interesting and indeed fundamental indications in these results. It has long been considered that soils under arid or semi-arid conditions contain more readily soluble material than soils from other regions. While, as shown by various investigators, the amount of water-soluble salts in such soils is often quite high, the data presented show that after this material is removed by washing, the rate of formation of soluble products is comparatively slow.

If the soils are grouped with respect to the precipitation to which they are subjected and an average freezing-point depression found for each group, taking into consideration the 5 and 10-day periods only, the data of table 2 are obtained.

Since some of the groups contain only a small number of soils and some contain a number of sands which appear to be less reactive than the heavier classes, too much significance cannot be attached to these averages. However, the data are quite suggestive in that soils from regions of quite low rainfall and from regions of excessive precipitation appear to have a lower rate of solubility than those from regions of intermediate precipitation.

TABLE 2

Comparative rate of solubility of soils from regions of different precipitation when maintained at 25°C.

ANNUAL PRECIPITATION	FREEZING-POINT DEPRESSION	
	5 days	10 days
	°C.	°C.
Below 20 inches.....	0.0067	0.0107
20 to 30 inches.....	0.0200	0.0287
30 to 35 inches.....	0.0114	0.0180
35 to 40 inches.....	0.0132	0.0200
40 to 50 inches.....	0.0120	0.0143

If a comparison is made between the soils derived from glacial material, the soils from the far west and the soils south of the glacial belt, the data of table 3 are obtained.

TABLE 3

Comparative rate of solubility of soils from the glaciated, western and southern portions of the United States, when maintained at 25°C.

	FREEZING-POINT DEPRESSION	
	5 days	10 days
	°C.	°C.
Western soils.....	0.0067	0.0107
Glacial soils.....	0.0129	0.0200
Southern soils.....	0.0148	0.0206

These results are interesting in that they show the western soils, or those chiefly formed by the processes of disintegration rather than of decomposition, are much slower in their rate of formation of soluble material than soils from the glaciated portions of the United States. This is somewhat at variance with earlier teachings.

It is also interesting to note that the glacial soils have practically the same rate of solubility as the soils from the unglaciated areas. This is also contrary to the generally accepted idea. There may be some doubt as to whether the soils from Kansas receiving approximately 30 inches of precipitation and those from Texas receiving a rainfall of only 21 inches should be put in the same group with the other southern soils which are subject to high precipita-

tion. Should these soils be omitted the results for the 5-day period become 13.9 instead of 14.8, and for the 10-day period 19.8 in place of 20.0. The inclusion of the data from these soils therefore makes no appreciable difference in the ultimate results.

Subsoils

The rate of formation of soluble material in a number of subsoils was studied in the same manner as described for the surface soils. The data obtained, together with the annual precipitation to which the soils are subjected, are presented in table 4.

TABLE 4

Rate of formation of soluble material in subsoils from different regions of the United States, when maintained at 25°C.*

	ANNUAL PRECIPITA- TION	FREEZING-POINT DEPRESSION					
		0 days °C.	5 days °C.	10 days °C.	30 days °C.	60 days °C.	
1. Cochise, Arizona.....	11.00	0.000	0.004	0.004	0.006	0.006	
2. Tucson, Arizona.....	12.00	0.008	0.030	0.028	0.035	0.043	
3. Nevada Agricultural College.....	8.30	0.000	0.008	0.008	0.010		
4. Whittier, California, clay loam 1 to 2 ft.....	13.00	0.001	0.002	0.003	0.007		
5. Riverside, California sandy loam 1 to 2 ft.....	10.00	0.000	0.003	0.002	0.003		
6. Lind, Washington.....	9.50	0.000	0.008	0.007	0.007	0.007	
7. Pullman, Washington.....	21.64	0.000	0.003	0.007	0.004	0.000	
8. Spur, Texas.....	21.00	0.000	0.007	0.024	0.017	0.012	
9. Lubbock, Texas.....	21.00	0.000	0.007	0.008	0.015	0.010	
9a. Lubbock, Texas, sub- soil 2.....	21.00	0.000	0.006	0.018	0.017	0.015	
33. Chillicothe, Texas.....	26.29	0.000	0.003	0.006	0.003	0.002	
<i>Franklin County, Ohio</i>							
40. Clyde silty clay loam	38.00	0.000	0.002	0.002	0.006	0.004	
41. Ellsworth silt loam.....	38.80	0.000	0.005	0.000	0.009	0.005	
42. Miami silty clay loam.....	38.80	0.000	0.008	0.009	0.011	0.017	
45. Lexington, Ken- tucky, 12 to 24 inches.....	44.80	0.000	0.005	0.005	0.006	0.002	
46. Greenville, Ken- tucky, 12 to 24 inches.....	45.80	0.000	0.001	0.004	0.003		
		0 days	1 day	4 days	10 days	20 days	40 days
							60 days
<i>Michigan soils</i>							
15. Miami silt loam.....	30.99	0.003	0.006	0.008	0.010	0.012	0.012
16. Miami silt loam.....	30.99	0.000	0.001	0.006	0.004	0.004	0.000
17. Miami very fine sandy loam.....	30.99	0.000	0.002	0.009	0.009	0.017	0.018
19. Clyde silt loam.....	30.99	0.000	0.005	0.011	0.011	0.012	0.008
20. Miami sandy loam.....	30.99	0.000	0.002	0.001	0.002	0.000	0.000

* Depth of sampling from 2 to 3 feet unless otherwise stated.

These data show that the rate of formation of soluble substances is quite slow in practically all subsoils regardless of the material from which they were derived or the climatic conditions to which they have been subjected. The only notable exception to this observation is the sample from Tucson, Arizona, and since this is a river-bottom soil the abnormal behavior is not surprising.

This lack of solubility of subsoils is of interest in the discussion of the question as to how much of their mineral plant-food elements plants draw from the lower strata of the soil. It also opens the question as to whether the greater solubility of material in the surface soil is due to the presence of organic matter or to a more advanced condition of decay of the mineral constituents.

Solubility of very old soils

In the classification of soils Professor Marbut lays much emphasis on age. There are in the United States certain areas of soil which are recognized as extremely old, that is, from the standpoint of weathering, and in the present study it was considered very desirable to include some such samples. The specimens used were furnished by the Bureau of Soils. The procedure was the same as described above.

TABLE 5

Rate of formation of soluble material in soils which have undergone extreme weathering, maintained at 25°C.

	FREEZING-POINT DEPRESSION					
	0 days	1 day	5 days	10 days	30 days	60 days
	°C.	°C.	°C.	°C.	°C.	°C.
48. Tennessee soils						
Lebanon silt loam						
Surface 8 inches.....	0.000	0.002	0.004	0.004	0.007	0.010
Subsoil 8 to 25 inches.....	0.000	0.001	0.003	0.002	0.003	0.002
49. Hagerstown silt loam 8 inches.....	0.000	0.003	0.008	0.010	0.009	0.011
50. Alabama soils						
Rushton fine sandy loam						
Surface 10 inches.....	0.000	0.000	0.000	0.004	0.004	0.000
Subsoil 10 to 36 inches.....	0.000	0.000	0.000	0.002	0.002	0.002
51. Orangeburg fine sandy loam 10 inches.....	0.000	0.000	0.000	0.000	0.000	0.900
Subsoil 10 to 36 inches.....	0.000	0.000	0.000	0.000	0.000	0.000

The data of table 5 are very interesting in that an extremely low solubility is shown. The indications are that soils may be less active because of lack of weathering on the one hand and extreme weathering on the other. The rate of formation of soluble substances in parent glacial material is being investigated and may throw additional light on this question.

Comparative solubility of the separates composing the various soil classes

In a study of the solubility of soils the question naturally arises whether the soluble material is derived from all the particles or largely from the smaller separates. To throw some light on this phase of the problem a number of soils were divided into their separates and the solubility of each group of particles determined by the same procedure as was used for the soils. The coarser separates were obtained by passing the soil through a series of screens. Each portion was thoroughly rubbed with a rubber-tipped pestle to insure the crushing of all crumbs. In addition, after placing the samples in the freezing tubes, all fine material was removed by thoroughly shaking with distilled water and decanting the turbid liquid. The very fine sand was separated from the silt and clay by sedimentation. The decanted liquid bearing the silt and clay was allowed to stand about 18 hours and the sediment taken for the portion designated as silt and clay. No attempt was made to separate the silt and clay since this would involve so much washing that it was feared the results would be vitiated. The writers realize that these separations were not perfect but are of the opinion that they were sufficiently accurate to warrant the conclusions drawn from the data.

Table 6 contains the data obtained for the 1, 4, 10, 20, 40, and 60-day periods.

An examination of the above data reveals the fact that all the separates except the silt and clay have a very low rate of solubility. Moreover, it seems that the sands from the arid regions are not appreciably more active in this respect than are those from others. Of course, larger numbers of soils should be run in order definitely to establish this point and additional information will be furnished later. In this connection the work of Failyer (3), Hall and Russell (4), Loughridge (5), Puchner (8), McCaughey and William (6) and others on the mineralogical and chemical composition of the separates from various soils, is of extreme interest.

This greater solubility of the finer separates may be due to one or more of several causes. Possibly the greater surface exposed by these minute particles explains the greater rate at which they give up material to solution. On the other hand, a considerable quantity of salts may be adsorbed by these bodies which are given up at various rates when the particles are subjected to treatment with pure water. That adsorption enters into the reaction is indicated by the reversion or decrease in the amount of soluble material after a maximum concentration has been reached, which is observed in many cases. It may be true also, that these smaller particles are more completely oxidized, hydrated, or "weathered," and therefore are in reality more highly soluble than the coarser particles.

TABLE 6.

Rate of formation of soluble material in the various separates composing a number of soils from different regions of the United States, maintained at 25°C.

	FREEZING-POINT DEPRESSION						
	0 days °C.	1 day °C.	4 days °C.	10 days °C.	20 days °C.	40 days °C.	60 days °C.
<i>Lubbock, Texas</i>							
Medium sand.....	0.000	0.000	0.004	0.008	0.009	0.006	0.007
Fine sand.....	0.000	0.003	0.005	0.010	0.013	0.012	0.009
Very fine sand.....	0.000	0.006	0.007		0.011	0.012	0.016
Silt and clay.....	0.000	0.005	0.018		0.030	0.027	0.025
<i>Spur, Texas</i>							
Coarse sand.....	0.000	0.000	0.002	0.006	0.007	0.008	0.012
Medium sand.....	0.000	0.000	0.001	0.005	0.008	0.008	0.011
Fine sand.....	0.000	0.000	0.001	0.005	0.013	0.009	0.011
Very fine sand.....	0.000	0.000	0.002	0.004	0.015	0.010	0.012
Silt and clay.....	0.000	0.008	0.012	0.020	0.021	0.021	0.016
<i>Franklin County, Ohio, Ellsworth silt loam</i>							
Coarse sand.....	0.000	0.000	0.000	0.000	0.003	0.003	0.006
Medium sand.....	0.000	0.000	0.003	0.000	0.003	0.001	
Fine sand.....	0.000	0.000	0.002	0.000	0.004	0.002	0.005
Very fine sand.....	0.000	0.002	0.003	0.005	0.005	0.004	0.005
Silt and clay.....	0.000	0.005	0.008	0.010	0.010	0.014	0.014
<i>Chillicothe, Texas</i>							
Coarse sand.....	0.000		0.000	0.000	0.000	0.005	0.004
Medium sand.....	0.000		0.007	0.001	0.010	0.004	0.002
Fine sand.....	0.000		0.000	0.006	0.002	0.003	0.003
Very fine sand.....	0.000		0.003	0.003	0.007	0.007	0.006
Silt and clay.....	0.000		0.009	0.019	0.019	0.017	0.009
<i>Pecos, Texas</i>							
Medium sand.....	0.000		0.011	0.010	0.010	0.011	0.012
Fine sand.....	0.000		0.012	0.002	0.017	0.014	0.016
Very fine sand.....	0.000		0.004	0.003	0.008	0.008	0.004
Silt and clay.....	0.000		0.012	0.021	0.020	0.018	0.009
<i>Lind, Washington</i>							
Medium sand.....	0.000	0.001	0.014	0.011			
Fine sand.....	0.000	0.001	0.009	0.006	0.007	0.009	0.010
Very fine sand.....	0.000	0.000	0.003	0.003	0.003	0.003	0.006
Silt and clay.....	0.000	0.010	0.010	0.014	0.024	0.023	0.023
<i>Pullman, Washington</i>							
Very fine sand.....	0.000	0.001	0.002	0.007	0.006	0.006	0.006
Silt and clay.....	0.000	0.011	0.010	0.018	0.028	0.029	0.033
<i>Chocise, Arizona, Sulfur Springs Valley dry farm</i>							
Coarse sand.....	0.000	0.000	0.004	0.006	0.008	0.006	0.006
Medium sand.....	0.000	0.002	0.005	0.007	0.008	0.008	0.008
Fine sand.....	0.000	0.002	0.006	0.007	0.008	0.008	0.008
Very fine sand.....	0.000	0.000	0.008		0.006	0.005	0.005
Silt and clay.....	0.000	0.000	0.009		0.017	0.025	0.028

TABLE 6—Continued

	FREEZING-POINT DEPRESSION						
	0 days	1 day	4 days	10 days	20 days	40 days	60 days
	°C.	°C.	°C.	°C.	°C.	°C.	°C.
<i>Tucson, Arizona, Rillito River bottom</i>							
Coarse sand.....	0.000	0.004	0.002	0.005	0.010	0.006	0.007
Medium sand.....	0.000	0.002	0.002	0.006	0.007	0.010	0.008
Fine sand.....	0.000	0.005	0.005	0.006	0.007	0.013	0.010
Very fine sand.....	0.000	0.000	0.003		0.005	0.007	0.006
Silt and clay.....	0.000	0.017	0.034		0.034	0.034	0.032
<i>Greenville, Kentucky</i>							
Very fine sand.....	0.000	0.002	0.004	0.004	0.004	0.006	0.006
Silt and clay.....	0.000	0.007	0.011	0.010	0.037	0.027	0.021
<i>Lexington, Kentucky</i>							
Coarse sand.....	0.000	0.000	0.001	0.005	0.007	0.005	0.007
Medium sand.....	0.000	0.000	0.002	0.003	0.006	0.003	0.007
Fine sand.....	0.000	0.000	0.001	0.006	0.006	0.004	0.008
Very fine sand.....	0.000	0.000	0.004	0.004	0.013	0.008	0.008
Silt and clay.....	0.000	0.005	0.009	0.011	0.032	0.021	0.021
<i>Michigan, Miami very fine sand</i>							
Coarse sand.....	0.000	0.000	0.000	0.003	0.002	0.000	0.003
Medium sand.....	0.000	0.000	0.000	0.000	0.003	0.001	0.002
Fine sand.....	0.000	0.000	0.000	0.000	0.004	0.000	0.001
Very fine sand.....	0.000	0.000	0.004	0.003	0.006	0.006	0.004
Silt and clay.....	0.000	0.000	0.015	0.020	0.021	0.019	0.012
<i>Michigan, Miami very light sandy loam</i>							
Coarse sand.....	0.000	0.000	0.001	0.000	0.003	0.002	0.003
Medium sand.....	0.000	0.003	0.000	0.001	0.001	0.000	0.003
Fine sand.....	0.000	0.000	0.002	0.004	0.003	0.000	0.001
Very fine sand.....	0.000	0.004	0.002	0.004	0.007	0.003	0.002
Silt and clay.....	0.000	0.001	0.007	0.018	0.027	0.015	0.011
<i>Michigan, Clyde light silt loam</i>							
Coarse sand.....	0.000	0.000	0.002	0.006	0.008	0.003	0.002
Medium sand.....	0.000	0.000	0.006	0.005	0.005	0.004	0.004
Fine sand.....	0.000	0.000	0.003	0.005	0.005	0.006	0.010
Very fine sand.....	0.000	0.000	0.009	0.010	0.025	0.017	0.014
Silt and clay.....	0.000	0.002	0.027	0.032	0.050	0.044	0.044
<i>Michigan, Miami silt loam</i>							
Coarse sand.....	0.000	0.000	0.000	0.000	0.002	0.003	0.005
Medium sand.....	0.000	0.000	0.000	0.000	0.001	0.003	0.007
Fine sand.....	0.000	0.000	0.000	0.001	0.004	0.004	0.008
Very fine sand.....	0.000	0.003	0.006	0.010	0.008	0.010	0.009
Silt and clay.....	0.000	0.020	0.021	0.028	0.029	0.033	0.014
<i>Michigan, Miami sandy loam</i>							
Coarse sand.....	0.000	0.002	0.002	0.003	0.002	0.003	0.008
Medium sand.....	0.000	0.000	0.002	0.001	0.003	0.004	0.007
Fine sand.....	0.000	0.003	0.001	0.002	0.003	0.005	0.008
Very fine sand.....	0.000	0.003	0.000	0.000	0.000	0.004	0.004
Silt and clay.....	0.000	0.012	0.024	0.022	0.036	0.037	0.038
<i>Nevada Agricultural College</i>							
Coarse sand.....	0.000		0.000	0.001	0.000	0.003	0.003
Medium sand.....	0.000		0.002	0.007	0.006	0.004	0.007
Fine sand.....	0.000		0.011	0.009	0.009	0.013	0.009
Very fine sand.....	0.000		0.012	0.002	0.006	0.008	0.011
Silt and clay.....	0.003		0.020	0.030	0.040		0.043

Effect of grinding on the solubility of the separates

In order to gain some idea of the cause of this greater solubility a number of the coarser separates were ground as finely as could be done conveniently. The grinding was done in a mill with steel burrs which was set so that all the material was small enough to pass a 200-mesh screen.

The separates to be ground were first washed with distilled water until the freezing-point depression was practically zero. As will be observed from the

TABLE 7

Effect of grinding the coarser separates on the rate of formation of soluble material, with the temperature maintained at 25°C.

SAMPLE AND SEPARATE GROUNDED	FREEZING-POINT DEPRESSION							
	0 days °C.	1 day °C.	3 days °C.	5 days °C.	10 days °C.	20 days °C.	40 days °C.	60 days °C.
<i>Lubbock, Texas</i>								
Medium sand.....	0.008	0.009	0.009	0.009	0.003	0.007	0.012	0.009
Fine sand.....	0.009	0.012	0.012	0.015	0.010	0.011	0.011	0.010
<i>Tucson, Arizona, river bottom</i>								
Medium sand.....	0.014	0.014	0.016	0.013	0.015	0.016	0.023	0.021
Fine sand.....	0.018	0.017	0.020	0.019	0.013	0.015	0.026	0.020
<i>Michigan very light sandy loam</i>								
Coarse sand.....	0.015	0.016	0.019	0.020	0.016	0.021	0.017	0.020
Medium sand.....	0.005	0.007	0.008	0.012	0.009	0.012	0.026	0.026
Fine sand.....	0.006	0.008	0.009	0.009	0.008	0.010	0.017	0.022
<i>Michigan very fine sand</i>								
Coarse sand.....	0.009	0.010	0.011	0.009	0.015	0.013		
Medium sand.....	0.006	0.008	0.009	0.011	0.008	0.009		
Fine sand.....	0.006	0.010	0.008	0.008	0.009	0.013	0.016	0.010
<i>Michigan loam</i>								
Coarse sand.....	0.006	0.011	0.014	0.013	0.012	0.011	0.015	0.014
Medium sand.....	0.009	0.012	0.015	0.016	0.012	0.012	0.012	0.012
Fine sand.....	0.009	0.009	0.016	0.013	0.012	0.016	0.016	0.020
<i>Michigan light silt loam</i>								
Coarse sand.....	0.011	0.013	0.017	0.019	0.018	0.021	0.017	0.024
Medium sand.....	0.012	0.011	0.019	0.019	0.018	0.019	0.015	0.028
Fine sand.....	0.008	0.010	0.015	0.015	0.013	0.015	0.018	0.018
<i>Michigan, Miami silt loam</i>								
Coarse sand.....	0.009	0.010	0.018	0.013	0.013	0.013		
Medium sand.....	0.006	0.008	0.008	0.008	0.008	0.012	0.010	0.010
Fine sand.....	0.009	0.010	0.009	0.010	0.010	0.014	0.017	0.018

data (table 7) an appreciable freezing-point depression was observed immediately upon the addition of distilled water, consequently this increased solubility must have been the direct result of grinding. When placed in the constant-temperature chamber further increase in concentration of the soil solution was slight even after 20, 40 or 60 days in most instances. It must be concluded, therefore, that grinding has affected the rate of solubility of the coarser separates, but the influence is not sufficient to warrant the statement that the greater solubility of the silt and clay portion is due entirely to a finer state of division.

Effect of treatment with sodium nitrate on the solubility of soil separates

In the work of Bouyoucos and Laudeman (2) it was found when soils were treated with various salts in solution and then washed until the concentration of the soil solution was practically zero, that the subsequent rate of formation

TABLE 8

Effect of treatment with 0.1 N NaNO₃ on the solubility of the coarser soil separates, maintained at 25°C.

	FREEZING-POINT DEPRESSION						
	0 days °C.	1 day °C.	4 days °C.	10 days °C.	20 days °C.	40 days °C.	60 days °C.
<i>Spur, Texas</i>							
Medium sand.....	0.000	0.009	0.008	0.012	0.011	0.022	0.026
Fine sand.....	0.000	0.008	0.011	0.012	0.014	0.028	0.027
Very fine sand.....	0.000	0.007	0.010	0.011	0.013	0.024	0.029
<i>Lubbock, Texas, 1</i>							
Medium sand.....	0.000	0.008	0.010	0.006	0.009	0.014	0.010
Fine sand.....	0.000	0.010	0.010	0.011	0.012	0.013	0.007
Very fine sand.....	0.000	0.008	0.012	0.012	0.014	0.017	0.003
<i>Ellsworth silt loam, Franklin County, Ohio</i>							
Very fine sand.....	0.000	0.009	0.009	0.011	0.010	0.010	0.008
<i>Lind, Washington</i>							
Very fine sand.....	0.000	0.008	0.007	0.009	0.010	0.007	0.009
<i>Pullman, Washington</i>							
Very fine sand.....	0.000	0.008	0.010	0.011	0.008	0.008	0.010
<i>Cochise, Arizona, dry farm</i>							
Coarse sand.....	0.000	0.003	0.002	0.005	0.006	0.008	0.010
Medium sand.....	0.000	0.008	0.007	0.010	0.008	0.007	0.012
Fine sand.....	0.000	0.008	0.007	0.010	0.008	0.008	0.012
Very fine sand.....	0.000	0.008	0.007	0.010	0.007	0.008	0.012
<i>Tucson, Arizona, river bottom</i>							
Coarse sand.....	0.000	0.006	0.010	0.014	0.018	0.018	0.020
Medium sand.....	0.000	0.007	0.012	0.013	0.015	0.014	0.015
Fine sand.....	0.000	0.007	0.013	0.014	0.015	0.017	0.014
Very fine sand.....	0.000	0.008	0.014	0.017	0.016	0.014	0.012
<i>Greenville, Kentucky</i>							
Very fine sand.....	0.000	0.011	0.010	0.010	0.008	0.016	0.015
<i>Lexington, Kentucky</i>							
Very fine sand.....	0.000	0.010	0.010	0.010	0.009	0.015	0.018
<i>Michigan soils</i>							
<i>Light silt loam</i>							
Coarse sand.....	0.000	0.001	0.009	0.009	0.009	0.008	0.004
Medium sand.....	0.000	0.000	0.008	0.009	0.010	0.008	0.006
Fine sand.....	0.000	0.003	0.008	0.011	0.011	0.009	0.008
Very fine sand.....	0.000	0.004	0.011	0.015	0.015	0.013	0.012
<i>Very light sandy loam</i>							
Coarse sand.....	0.000	0.003	0.003	0.003	0.007	0.001	0.003
Medium sand.....	0.000	0.002	0.003	0.003	0.006	0.001	0.002
Fine sand.....	0.000	0.002	0.003	0.003	0.006	0.002	0.004
Very fine sand.....	0.000	0.002	0.008	0.009	0.010	0.005	0.008

TABLE 8—Continued

	FREEZING-POINT DEPRESSION						
	0 days °C.	1 day °C.	4 days °C.	10 days °C.	20 days °C.	40 days °C.	60 days °C.
Very fine sand							
Coarse sand.....	0.000	0.001	0.001	0.003	0.006	0.008	0.004
Medium sand.....	0.000	0.002	0.003	0.003	0.007	0.007	0.005
Fine sand.....	0.000	0.003	0.004	0.003	0.006	0.007	0.006
Very fine sand.....	0.000	0.003	0.008	0.007	0.009	0.009	0.006
Loam							
Coarse sand.....	0.000	0.005	0.008	0.007	0.008	0.009	0.012
Medium sand.....	0.000	0.005	0.007	0.007	0.009	0.007	0.009
Fine sand.....	0.000	0.009	0.007	0.007	0.010	0.008	0.008
Very fine sand.....	0.000	0.008	0.009	0.006	0.012	0.010	0.012
Silt loam							
Coarse sand.....	0.000	0.001	0.000	0.007	0.003	0.005	0.003
Medium sand.....	0.000	0.003	0.004	0.007	0.004	0.007	0.002
Fine sand.....	0.000	0.000	0.003	0.006	0.003	0.006	0.006
Very fine sand.....	0.000	0.006	0.003	0.009	0.006	0.010	0.008

of soluble material was much affected. Some salts markedly increased the rate of solubility while others decreased it. Of the salts tested, sodium nitrate was found to be most active in increasing the rate of solution. It was determined, therefore, to treat the coarser separates of a number of soils with a solution of sodium nitrate. The procedure was as follows. The separates were allowed to stand 24 hours in an 0.1 *N* solution of sodium nitrate, after which they were washed with distilled water until the freezing-point depression was practically zero. The samples were then placed in tubes in a 25°C. chamber and the freezing point determined at given intervals in the usual manner.

The formation of soluble material is evidently stimulated by treatment with NaNO_3 . This is not only true for the very fine sand but also for the coarser separates such as a medium sand. The action seems to be quite rapid, as in most cases the major part of the increase occurs within 24 hours. In the case of some soils, however, the effect is more or less continuous to the end of the 60-day period. In general, the separates from the western soils were affected somewhat more than the others studied.

SUMMARY

Comparative rates of formation of soluble substances in surface and subsoils collected from widely separated areas in the United States have been made. Contrary to popular belief it cannot be said from these results that soils formed under conditions of low precipitation are more soluble than are those that have proceeded somewhat farther in their weathering. Samples of soil taken from formations that have undergone extreme weathering are very inert. It seems, therefore, that so-called new soils are less active than those somewhat older, and the aged soils are almost inert.

The subsoils taken from all regions formed soluble salts very slowly. Our investigations on the soluble-salt content of soils at different depths and periods of the growing season have shown also that there is very little activity in field soils below six inches, that is, in the vicinity of East Lansing, Michigan.

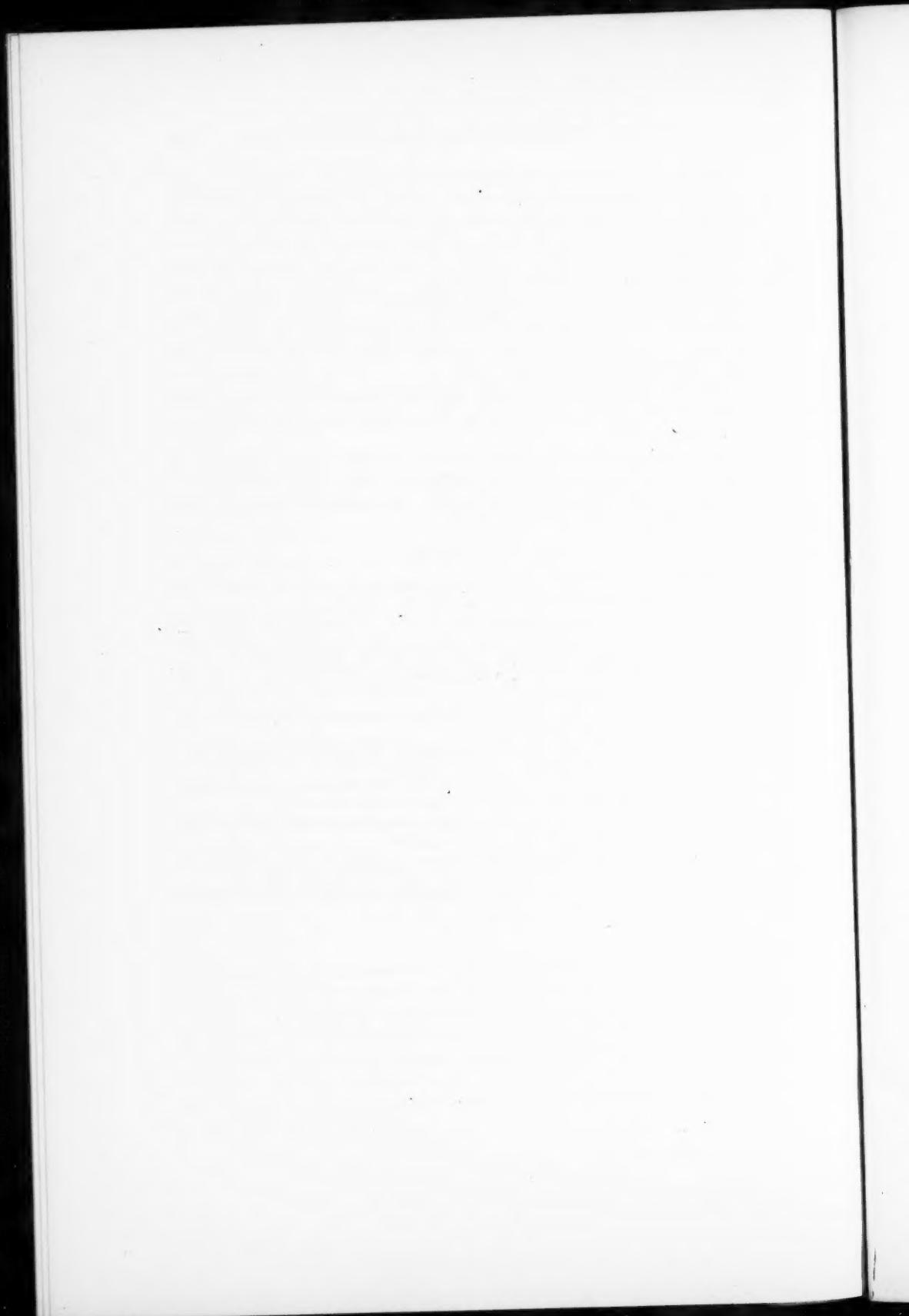
Soil separates comprising a number of soils have been isolated and their activities determined. These results bring out that the finer separates, silt and clay, are responsible chiefly for the formation of soluble salts in the samples of soils under investigations. The sandy particles are very inactive and it cannot be concluded that those taken from soils of arid regions are notably less so than are the others investigated.

Grinding the separates measurably increased their solubility. Usually only slight increases in the material going into solution were observed after the first 24-hour period.

When the separates were treated with 0.1 *N* NaNO₃ and then washed until free of soluble material the rate of formation of soluble substances was measurably affected. Those from the western soils responded somewhat more than the others.

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THE EFFECT OF CERTAIN ENVIRONMENTAL CONDITIONS ON THE RATE OF DESTRUCTION OF VANILLIN BY A SOIL BACTERIUM

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One of the theories to explain why soils are or become infertile is the soil toxin theory which assumes that the failure of crops to grow on a soil is due to the presence of organic material in the soil which is injurious to the plants. Organic compounds exceedingly injurious to plants have been isolated from the soil. Among these compounds are the aldehydes, vanillin (10) and salicylic aldehyde (9). It has been shown that in at least some Alabama soils, the addition of vanillin has almost no injurious effects on plants (3) because it is rapidly destroyed by soil bacteria (4). It has also been shown that this is true of other soils to which the addition of vanillin has little or no effect on the growth of plants (6). It is true of some soils, however, that although the vanillin-destroying bacteria are present, added vanillin will persist and evidence its injurious effects on the growth of plants for a considerable period of time (6, 11). This persistence must be due to conditions which prevent the bacteria from acting on vanillin. In the present paper a study is made in solution cultures of the effect of certain conditions such as acidity, alkalinity, aeration and mineral salts on the decomposition of vanillin. The experimental work was performed in 1916 and the results, though fragmentary, are presented because conditions have prevented further investigation by the writers.

In order to study this question the vanillin-destroying bacterium isolated from Alabama soil was grown in synthetic culture solutions. What appears to be the same organism has also been isolated from Nebraska, New York and Virginia soils.

No complete study of this organism has been made. It is characterized by its ability to destroy vanillin and by its growth on beef-extract agar. On beef-extract agar, plus 1, it produces a cheesy yellow growth, wrinkled on the surface, and stains the medium yellow. It is aerobic, liquifies gelatine, grows moderately on potato and develops in peptone solutions containing dextrose, lactose, saccharose or glycerine without gas formation. It clears milk without coagulation.

No attempt has been made to determine how many species of bacteria there are which destroy vanillin. Two species have been isolated from the

soil, the one already referred to above and a second which produces no pigment on beef-extract agar. It is believed, however, that the ability to destroy vanillin is not a common property of soil bacteria and that the number of species which have the ability is limited.

DETERMINATION OF VANILLIN

Early in the study of the action on vanillin of the vanillin-destroying bacterium described above, it was found that the determination of the amount of vanillin by the method used was unreliable. The method first used was that described by Folin and Denis (2) with clarification by the lead acetate omitted. This method requires a reagent composed of phosphoric acid, sodium tungstate and phospho-molybdic acid and is referred to by them as the phenol reagent. On the addition of a saturated sodium carbonate solution, it produces with vanillin a deep blue solution, the depth of the color varying directly with the amount of vanillin present. Using the phenol reagent to determine the amount of vanillin in a synthetic nutrient solution in which the vanillin-destroying bacterium had grown, it was sometimes found that apparently more vanillin was present after the action of the bacterium than had been originally added. In some cases, twice as much vanillin was apparently formed in the inoculated culture as was present in an uninoculated, or check culture.

In an attempt to clear up this contradiction, the acid nitrate of mercury described by Estes (1) was used for determining vanillin. This reagent produces with vanillin a pink color, the depth of color varying directly with the amount of vanillin present. It was found that, determined by this means, the amount of vanillin progressively decreased in a synthetic nutrient solution containing vanillin and inoculated with a pure culture of the vanillin-destroying bacteria.

On further investigation, it was found that the anomalous results secured by the use of the phenol reagent were due to the fact that the bacterium oxidizes vanillin to vanillic acid (5) which produces a blue color with the phenol reagent 1.5-2.0 times as strong as is produced by an equal amount of vanillin. The depth of color yielded by a mixture of vanillin and vanillic acid with the phenol reagent, therefore, is the result of the color produced by both the vanillin and vanillic acid. The color production of vanillic acid with the Estes reagent however, is very slight so that vanillin can be determined in a mixture of vanillin and vanillic acid by the use of that reagent. Acid nitrate of mercury was therefore used for the determination of vanillin in the experiments reported below.¹

¹ It is probable that, by the use of lead acetate, a solution containing both vanillin and vanillic acid could be freed of the vanillic acid as it is precipitated by lead acetate in the presence of ammonia. The phenol reagent could then be used for the determination of the vanillin.

EFFECT OF ACIDITY AND ALKALINITY ON THE DECOMPOSITION OF VANILLIN

In determining the effect of acidity and alkalinity on the destruction of vanillin, the following nutrient solution was used:

K ₂ SO ₄	0.0340 gm.
NaNO ₃	0.1000 gm.
CaH ₄ (PO ₄) ₂	0.0710 gm.
Distilled Water.....	3000 cc.
Vanillin.....	As indicated

The solution was neutralized to phenolphthalein with NaOH, and aliquot parts made acid and alkaline with HCl and NaOH as noted in table 1. Forty cubic centimeters of solution were placed in 150-cc. Erlenmeyer flasks and after sterilization, 10 cc. of a sterile vanillin solution were added to each flask.² The organisms were allowed to grow 4 days at room temperature when the vanillin was determined by means of the acid nitrate of mercury reagent. Previous to the determination of the vanillin, the contents of each flask were neutralized.

TABLE 1
Effect of HCl and NaOH on the decomposition of vanillin

ADDITIONS PER 100 CC. OF SOLUTION	VANILLIN REMAINING IN CULTURE SOLUTION AT END OF 4 DAYS
	<i>p.p.m.</i>
10 cc. 0.1 N NaOH.....	260.0
5 cc. 0.1 N NaOH.....	41.6
2 cc. 0.1 N NaOH.....	24.0
1 cc. 0.1 N NaOH.....	23.6
Neutral to phenolphthalein.....	28.0
1 cc. 0.1 N HCl.....	274.0
2 cc. 0.1 N HCl.....	226.0
Checks, uninoculated.....	241.6

In this experiment which is the average of duplicate cultures, 1 cc. of 0.1 N HCl per 100 cc. was sufficient to inhibit the growth and action of the bacterium on vanillin. Between 5 and 10 cc. of 0.1 N NaOH were required, however, to stop its action. In this connection, it should be noted that Skinner and Noll (12) report that on unproductive soil the toxic effects of vanillin are overcome by liming. Truog and Sykora (13) also found that in an infertile acid sand, the poisonous action of the vanillin was greatly lessened by the addition of lime. A study of the relation of hydrogen-ion concentration to the decomposition of vanillin in solution cultures and sand should be made.

² This method of adding vanillin in solution after sterilization was used throughout when quantitative work was done, as it eliminated any danger of lack of uniformity in vanillin content of the flasks due to sterilization.

EFFECT OF AERATION ON THE RATE OF DECOMPOSITION OF VANILLIN

While studying the formation of the decomposition products of vanillin, it was observed that in a 2-liter Erlenmeyer flask containing 250 cc. of nutrient solution, the vanillin as tested for by the acid nitrate of mercury would disappear in three or four days. In the same flask, however, containing 1000 cc. of solution, vanillin was present after 3 weeks. The depth of solution in this case was about 7 cm. This difference was thought to be due to aeration. It should be noted, however, that the flask in which the slower digestion occurred had four times as much vanillin in it though the concentrations were the same.

To determine more definitely the effect of the depth of the solution on the rate of the disappearance of vanillin under the action of the vanillin-destroying bacterium, experiments were conducted in which 50 cc. of nutrient solution, made -0.2 Fuller's scale with NaOH, were placed in 2.5 by 25-cm. test-tubes and 150-cc. Erlenmeyer flasks. The quantity and composition of

TABLE 2
Effect of aeration on the rate of digestion of vanillin
Depth of solution in flask about 2 cm., in tube about 12 to 14 cm.

TIME FROM INOCULATION	VANILLIN IN FLASK		VANILLIN IN TUBE	
	Check not inoculated	Inoculated	Check not inoculated	Inoculated
days	p.p.m.	p.p.m.	p.p.m.	p.p.m.
3	242	108	226	190
5	210	24	220	78
7	306	8	292	40
9	234	0	224	34
11			246	14

the solution in both tubes and flasks were identical but in the tubes the depth of solution was 12 to 14 cm. with a diameter at the surface of the liquid of 2.5 cm. while in the flask the depth was about 2.0 cm. and the diameter at the surface of the liquid was 6.5 cm.

It is evident from the data in table 2 that the depth of the solution and the area of liquid surface exposed affect the rate of the decomposition of vanillin by this bacterium. The more rapid decomposition occurs in the flask where the depth of the solution is one-sixth of that in the tube and the liquid surface exposed is $2\frac{1}{2}$ times as great. This difference is no doubt due to the freer supply of oxygen offered in the case of the flask and is what would be expected when the destruction of vanillin by the organism is known to be an oxidative process.

THE EFFECT OF FERTILIZER SALTS ON THE DECOMPOSITION OF VANILLIN

It has been shown by Schreiner and Skinner (8) that fertilizer salts affect the toxicity of vanillin to wheat. The effects of calcium acid phosphate, sodium nitrate and potassium sulfate singly and in many combinations on

the toxicity of vanillin were studied by these investigators. The growth of wheat plants in culture solutions respectively high in phosphate, nitrate or potash and containing vanillin, showed that the vanillin depressed the growth least in the cultures high in nitrate and most in the cultures high in potash.

The writers have attempted to discover whether the same fertilizer salts have any effect on the rate at which vanillin is decomposed by the bacterium used in this investigation. The triangular diagram as used in physical chemistry was employed and the results are presented by its means. Monobasic calcium acid phosphate, sodium nitrate and potassium sulfate were used in 15 different combinations and in such concentrations that each culture solution contained a total concentration of 80 parts per million of P_2O_5 , NH_3 and K_2O . The mineral combinations used in parts per million of K_2O , P_2O_5 and NH_3 were as follows:

	K_2O	P_2O_5	NH_3
1	0	80	0
2	0	60	20
3	0	40	40
4	0	20	60
5	0	0	80
6	20	60	0
7	20	40	20
8	20	20	40
9	20	0	60
10	40	40	0
11	40	20	20
12	40	0	40
13	60	20	0
14	60	0	20
15	80	0	0

In preparing the culture solution sufficient of each of the three chemically pure salts was dissolved in distilled water to produce solutions containing 100 parts per million of P_2O_5 and K_2O , respectively.

This required:

- 0.1776 gm. of $CaH_4(PO_4)_2 \cdot H_2O$ per liter
- 0.5000 gm. of $NaNO_3$ per liter
- 0.1852 gm. of K_2SO_4 per liter

To prepare solution no. 1, 40 cc. of the $CaH_4(PO_4)_2$ were placed in a 150-cc. Erlenmeyer flask and after sterilization 10 cc. of a sterile vanillin solution were added, making a total of 50 cc. To prepare solution no. 7, 10 cc. of the K_2SO_4 , 20 cc. of the $CaH_4(PO_4)_2$ and 10 cc. of the $NaNO_3$ stock solution were placed in a 150-cc. Erlenmeyer flask and after sterilization, 10 cc. of a sterile vanillin solution were added.

Three separate experiments were performed. In each experiment the combinations of $CaH_4(PO_4)_2$, K_2SO_4 and $NaNO_3$ noted above were used. The

concentration of vanillin was uniform throughout a series. In experiment 1 (see table 3), 150-cc. Erlenmeyer flasks containing 50 cc. of solution were used and the concentration of vanillin was 508 parts per million. In experiment 2, the same containers and amount of solution were used but the experiment was performed in duplicate and the concentration of vanillin was 296 parts per million. In experiment 3, 50 cc. of solution were used in test-tubes approximately 2.5 by 25 cm. and the concentration of vanillin was 260 parts per million. Growth occurred at room temperature, the time varying with the experiment from 3 to 5 days. At the close of the experiment, the residual vanillin was determined by means of the acid nitrate of mercury reagent.

TABLE 3
Effect of fertilizer salts on the rate of decomposition of vanillin

SOLUTION	VANILLIN REMAINING IN CULTURES			
	Experiment I p.p.m.	Experiment II p.p.m.	Experiment III p.p.m.	Average p.p.m.
1	48.0	148.0	37.0	77.6
2	18.8	108.0	60.0	62.3
3	16.8	102.0	100.0	72.9
4	32.0	114.0	96.0	80.6
5	19.2	180.0	128.0	109.1
6	56.4	110.0		83.2
7	40.4	116.0	62.0	72.8
8	167.6	118.0	118.0	134.5
9	164.0	152.0	80.0	132.0
10	532.0*	106.0	188.0	147.0
11	Trace	130.0	254.0*	65.0
12	176.0	160.0	228.0	188.0
13	80.0	146.0	36.0	87.3
14	54.0	242.0	12.0	102.7
15	160.8	146.0	156.0	154.3
Checks	508.0	296.0	260.0	354.7

* No decomposition. Omitted from averages.

The results indicate that the decomposition of vanillin proceeds most rapidly in those combinations of salts high in $\text{CaH}_4(\text{PO}_4)_2$. The complete data are given in table 3 where the amount of vanillin in parts per million remaining in each culture solution at the end of the experiment is given.

Using the averages for the three experiments given in column 4 of table 3, the total of the amounts of vanillin remaining in all those combinations of salts containing 50 per cent of $\text{CaH}_4(\text{PO}_4)_2$ or more, is 515.8 parts per million; in all those combinations of salts containing 50 per cent of NaNO_3 or more, is 717.1 parts per million; and in all those combinations containing 50 per cent of K_2SO_4 or more, is 744.3 parts per million.

It is evident that the decomposition of vanillin in these experiments proceeds most rapidly in the cultures high in $\text{CaH}_4(\text{PO}_4)_2$ and least rapidly in

the cultures high in K_2SO_4 . This fact is shown graphically in figure 1. The 15 cultures are here arranged on the triangular diagram. Each circle on the diagram represents a culture, the upper numbers indicating the solution and the lower numbers the amount of vanillin remaining in the solution after the action of the bacteria. The solutions at the corners of the diagram contain one salt only; cultures 1, 5 and 15 containing $CaH_4(PO_4)_2$; $NaNO_3$ and K_2SO_4 , respectively. The cultures on the sides of the diagram contain combinations of two of

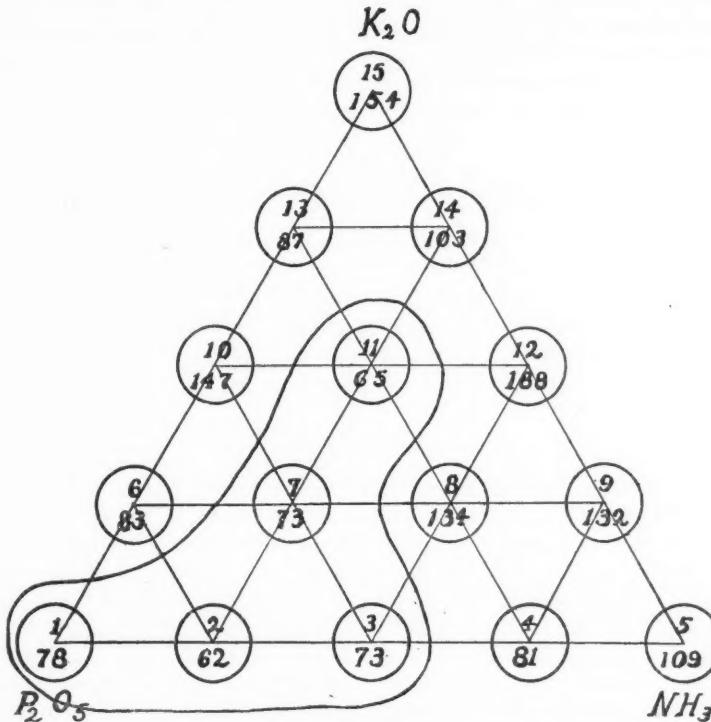


FIG. 1. TRIANGULAR DIAGRAM SHOWING THE EFFECT OF FERTILIZER SALTS ON THE RATE OF DECOMPOSITION OF VANILLIN

the salts and the cultures within the diagram contain combinations of the three salts in the proportions indicated earlier. An examination of the amounts of residual vanillin in the cultures shows that the smallest amounts are located in the corner of the triangle where the concentration of phosphate is highest. This is indicated in the figure by surrounding all those cultures containing less than 80 parts per million of residual vanillin by a line.

Although the effect of $CaH_4(PO_4)_2$ on the rate of decomposition of vanillin is marked, it is impossible at the present stage of the investigation to state

the cause of its effect. Several explanations are possible. It may be that the balancing effect of the calcium on the other salts in the solution permits a greater growth of the bacteria and therefore greater digestion of vanillin in those solutions high in calcium. It may be a specific effect of the phosphate radical. The decomposition of vanillin by this organism is an oxidative process. Schreiner and Sullivan (7) have shown that phosphates and nitrates increase the oxidative power of roots. In this connection it is interesting to note that the same investigators in studying the effect of the addition of sodium nitrate, potassium sulfate and calcium acid phosphate to the soil on the oxidative power of the soil, found that of the three salts acid calcium phosphate produced the greatest increase in oxidation in four soils out of five (table 15) and was greatest or second greatest in effect in all but one trial with a second lot of four soils (table 14).

EFFECT OF GLUCOSE ON THE DECOMPOSITION OF VANILLIN

To determine whether the presence of an easily fermentable carbohydrate such as glucose would affect the action of the bacterium on vanillin, experiments were conducted in synthetic nutrient cultures to which both vanillin and glucose had been added. It was found that the vanillin and glucose were used by the bacterium simultaneously and that the effect of the glucose on the destruction of vanillin was not marked.

DISCUSSION

In the work of which the present paper is the fourth report, we have tried to determine why organic toxic compounds were injurious to plants when added to some soils but not injurious when added to others. Previous investigators have assigned the more important role in the amelioration of the toxic effect of organic compounds to the physical action of the soil, to the chemical reactions which take place in the soil between the toxins and soil constituents or to the oxidative and reducing ability of plant roots. We have found that by far the most important role in the amelioration of the toxicity of organic compounds in the soil is played by the destructive action of soil microorganisms; in some cases by the action of specific bacteria. It is a well recognized fact that the ability to destroy some organic compounds is not a common property of all bacteria but for many organic compounds there are a limited number of species which have the power of destroying them. The complete disintegration of a mass of dead plants or animals is not accomplished by one species of microorganisms but is accomplished by the successive action of many. One group acts on the end-products of another. If at any stage the suitable organisms are not present or conditions are such that they cannot act, then the material which they usually break down will accumulate. This accumulation may be only temporary, disappearing with a change in conditions, or it may be more permanent, as in humus formation and the

formation of peat. But in any case, the destruction or accumulation is basically a function of the action of microorganisms.

While it is impossible to apply too strictly to the soil the results from solution cultures, we have shown in the present paper that alkalinity and good aeration favor the destruction of vanillin, because of their effect on the action of the vanillin-destroying bacteria on vanillin. We have also shown that some of the salts commonly used as fertilizer elements affect the rate at which vanillin is destroyed by bacteria. If it can be shown that the opposite conditions, acidity, poor aeration and the abundance or deficiency of some mineral salts allow the formation of vanillin to proceed, then the conditions for its accumulation and action as a factor in soil fertility are defined.

SUMMARY

1. It is believed that the number of species of soil bacteria able to destroy vanillin is limited.
2. Slight concentrations of HCl inhibit the action on vanillin of the soil bacterium studied.
3. Aeration favors the destruction of vanillin by the organism used.
4. In solution cultures containing $\text{CaH}_4(\text{PO}_4)_2$, NaNO_3 and K_2SO_4 singly or in combination and inoculated with the bacterium used, vanillin is destroyed most rapidly in those solutions high in $\text{CaH}_4(\text{PO}_4)_2$ and least rapidly in the solutions high in K_2SO_4 .
5. The presence of glucose has no marked effect on the rate at which vanillin is destroyed by the bacterium used.

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NOTES ON THE CONFERENCE ON ELEMENTARY SOIL TEACHING,
HELD AT LEXINGTON, KENTUCKY, JUNE, 1920

P. E. KARRAKER, *Secretary*

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Representatives of the agronomy or soils departments of sixteen state agricultural colleges met at the University of Kentucky on June 23, 24, and 25 to discuss the teaching of the first, or general, soil courses. The entire field of the teaching of these courses was considered but the attention of the conference was directed in particular to the securing of greater uniformity in the giving of the work in the various colleges and to the determination of what should properly constitute the laboratory part of this work.

The conference unanimously recommended that the first, or elementary, soils work should be given in a uniform general course dealing largely with the scientific principles underlying the successful management of soils with such practical application as good teaching and local conditions demand; this course to be required of all agricultural students, to be taken in the sophomore year when practicable, and to carry approximately 5 semester hours credit.

The minimum prerequisites recommended for this course were one year of general inorganic chemistry, one term of general geology and either high-school or college physics.

Further recommendations were that the subject matter of the course should be presented in well correlated lecture, recitation and laboratory work, that at least three-fifths of the time should be spent in lecture and recitation, and that it is desirable that a standard text book be used.

A suggested general outline of laboratory exercises was worked out. In this outline, for the most part, the common stock exercises are omitted. Exercises involving mainly quantitative work also are largely omitted if the laboratory work is confined to one credit hour per week.

The advantages of such a course, as brought out in the discussion, are that the student is enabled to obtain a survey of the entire subject in one course, that the preparation of standard text books, illustrative material, and standard laboratory equipment will be made possible and that transfer of credits from one institution to another will be facilitated.

The institutions represented at the conference were: University of Maryland, Georgia State College of Agriculture, Louisiana State University, University of Kentucky, Pennsylvania State College, University of Tennessee, Cornell University, Montana State College, University of Missouri, University of Illinois, A. & M. College of Texas, Michigan Agricultural College, University of Vermont, Ohio State University, Virginia Polytechnic Institute, University of Nevada.

